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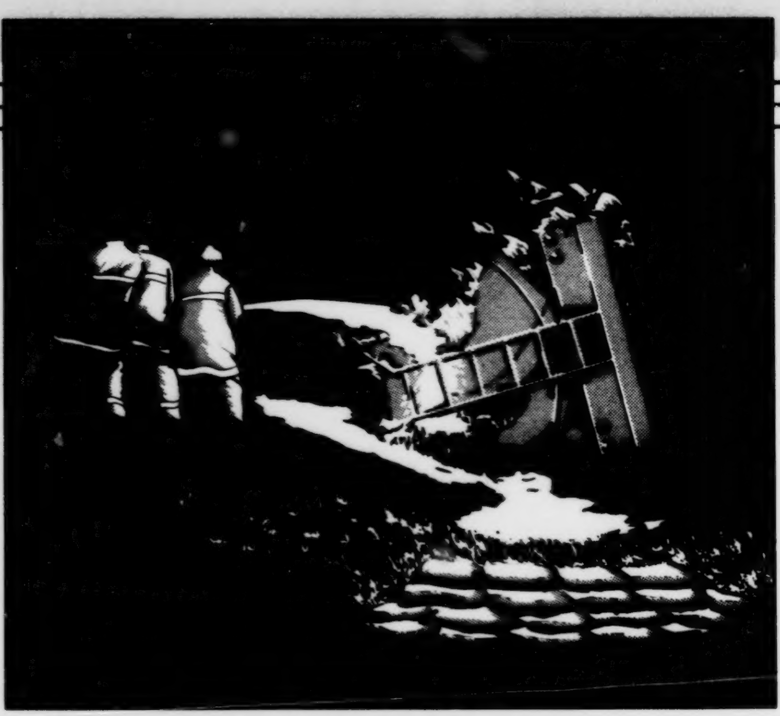

4th / 4ième

Technical Seminar on Chemical Spills

Colloque technique sur le déversement de produits chimiques

February 10-12, 1987
Toronto, Ontario

10 au 12 février 1987
Toronto, Ontario

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PROCEEDINGS

4th Technical Seminar
on Chemical Spills

February 10-12, 1987
Sheraton Centre
Toronto

Seminar sponsored by

Technology Development and
Technical Services Branch
Environmental Protection
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Environment Canada

COMPTES RENDUS

4ième Colloque technique sur le
déversement de produits chimiques

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Colloque commandité par

Direction du développement
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MODELLING OF THE SPREADING OF CHEMICAL SPILLS ON GRASS AND IMPERMEABLE SURFACES

by

R.L. Belore(1) and E.A. McBean(2)

ABSTRACT

Two- and three-dimensional spill models of the spread of liquids on land, are developed. Evaporative and infiltrative fluxes are estimated as losses of liquid, in combination with the surface affinity depth and position-computing methods to develop time-varying spill profiles.

Physical modelling results are used to demonstrate the validity of the computer model. Sensitivity tests of the model are provided.

INTRODUCTION

The frequency of spills of hazardous liquids has necessitated the development of modelling tools for predicting the spread of liquids over surfaces. The spreading of a chemical greatly affects both the evaporative flux and the infiltrative flux of the chemical into the soil. A poor prediction of the chemical's pool size (by an inappropriate spreading model) results in inaccurate estimates of potential health hazard zones surrounding the spill site which, in turn, could lead to inappropriate, or even dangerous action, by response personnel.

---

(1) Engineer, S.L. Ross Environmental Research, 346 Frank Street, Ottawa, Ontario, K2P 0Y1

(2) Professor, Department of Civil Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1

The intent of this paper is to describe a spill model for predicting the areal extent of spill movement. The model results are compared with physical modelling experiments. Sensitivity analyses are used to identify parameters to which the model is most sensitive.

BASICS OF THE SPILL PROCESS

In schematic form, the elements of the spill process are as indicated in Figure 1. Presuming a vertical spill, there is a region of supercritical flow emanating away from the point of impingement. If the surface is not sloped to a large extent (to be defined more fully later), the region of supercritical flow is followed by an hydraulic jump, a transition to more quiescent, or subcritical flow. The sloped surface of the spill profile provides the forcing function to move the leading edge or "bore" from the source of the spill. The depth at the bore, also frequently referred to as the surface affinity depth, is the result of surface tension between the liquid being spilled, and the underlying surface.

The above-mentioned elements, to varying degrees of sophistication, are reflected in models developed to describe the spill process. Wall (1984) developed a very complicated numerical model, but did not include the surface tension force at the leading edge. Abbott (1966), Fay (1969), Hoult and Suchon (1970) and Fannelop and Waldman (1971) developed analytic models to quantify the spreading of oil over calm water. Raj and Kalelkar (1974) adapted the Fannelop and Waldman (1971) solution to the spreading of viscous liquids over solids. This model assumes an instantaneous spill, the sudden release no longer influences the motion of the spill, and there is no evaporation or infiltration from the pool.

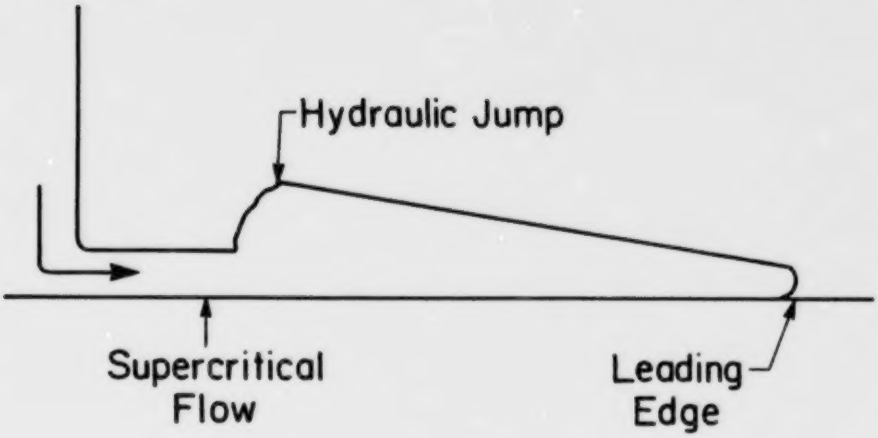
Hydraulic Jump
Supercritical Flow
Leading Edge

Figure 1 Elements of the Spill Process

Tanner (1979) developed some analytical models for drop formation on horizontal surfaces. Raisbeck and Mohtadi (1974) developed a model to simulate the spread of petroleum products over both permeable and impermeable Arctic soils, assuming that the slick reaches, and maintains, its equilibrium height. For viscous liquids, the assumption of a constant pool thickness may not be justified.

Component of Spill Model

The following elements were included in the spill model developed:
(i) the surace affinity depth controls the liquid depth at the bore, or leading edge;

(ii) frictional resistance arising from the fluid passing over the surface is characterized by Manning's equation;

(iii) subsets (i) and (ii) refer to momentum aspects of the spill process. The additional stipulation is the preservation of continuity - the quantity spilled must be evaporated, infiltrated, or still be within the spill profile. Considerations of (i) through (iii), while retaining a relatively simple model, are developed in the following manner for each time increment of calculation:

- the extent of the spill excursion is estimated. The calculations proceed by computing back from the surface affinity depth toward the origin of the spill, reflecting the increased depth necessary to overcome surface frictional resistance. Simultaneously, evaporative and infiltrated fluxes are removed from the spill as losses of fluid. The profile calculation proceeds, using the position-computing method for the standard step backwater calculation (e.g. see McBean and Perkins (1975)), until the law of conservation of mass is satisfied wherein:

$$\begin{array}{c} \text{volume of} \\ \text{fluid released} \\ \text{to the spill} \end{array} = \begin{array}{c} \text{volume of} \\ \text{fluid within} \\ \text{the spill} \\ \text{profile} \end{array} + \begin{array}{c} \text{volume lost} \\ \text{to} \\ \text{evaporation} \end{array} + \begin{array}{c} \text{volume lost} \\ \text{to} \\ \text{infiltration} \end{array}$$

The input data requirements for the model are detailed in Table 1.

Table 1 Description of Input Data Requirements for the Mathematical Model

Parameter	Commentary
surface tension,	- a function of liquid and solid surface
density of fluid,	
viscosity of fluid	
contact angle,	- angle between the fluid and solid surface
slope	- of solid surface
Manning coefficient, n	- a measure of frictional resistance of solid surface

NOTE: other parameters to the model relate to numerical and spatial/temporal aspects of solutions to the equations.

Physical Modelling

Experimental work was conducted in the relatively large-scale test bed illustrated in Figure 2. The tests included the addition of chemical to both horizontal and sloped surfaces. For the horizontal tests, the liquid source was applied to the centre of the surface with measurements then taken at both sides of the source for duplication of measurements. In the sloped tests, the chemical was applied to the elevated end of the platform with measurements made downstream from the source.

Two surface types were studied during testing. Plywood was utilized to simulate an impermeable surface because of its logistical

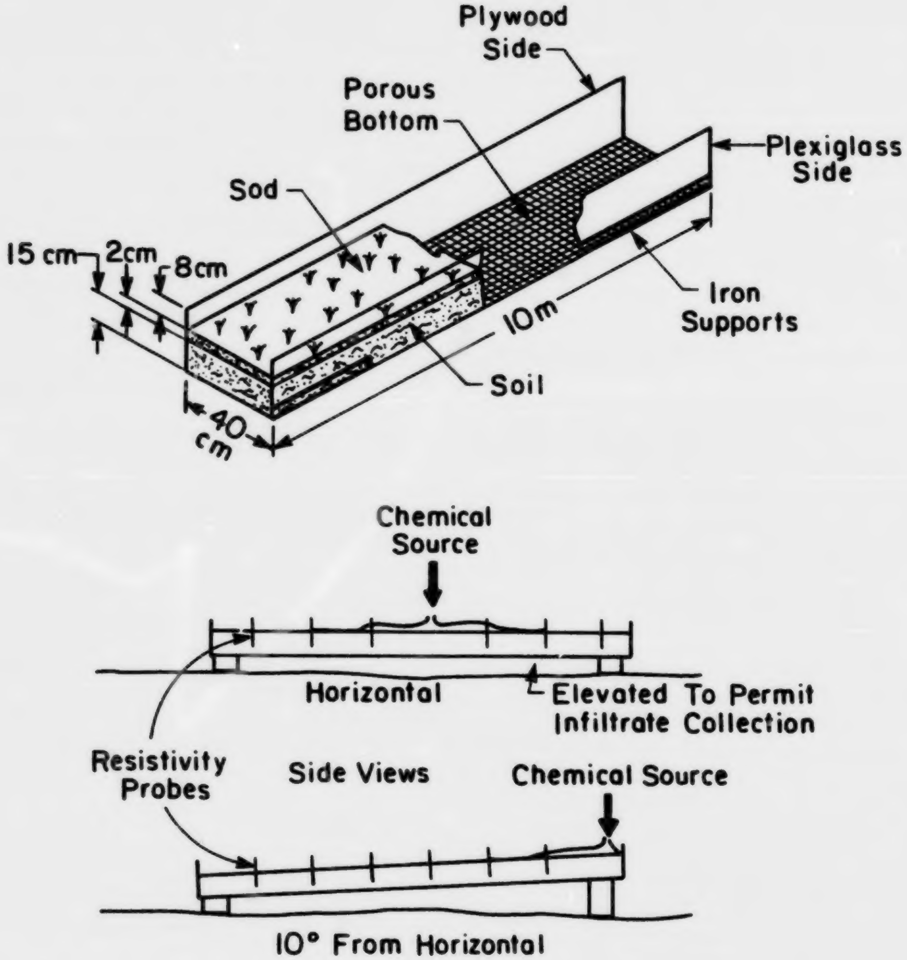
Plywood Side
Porous Bottom
Plexiglass Side
Sod
15 cm
2cm
8cm
Iron Supports
10m
Soil
40 cm
Chemical Source
Horizontal
Elevated To Permit Infiltrate Collection
Resistivity Probes
Side Views
Chemical Source
10° From Horizontal

Figure 2 Physical Modelling Facility

advantages and the consistent roughness which it provides. The second surface studied was natural sod placed over a loosely-packed topsoil.

Water was the primary "chemical" used in the tests. In order to evaluate the effects of viscosity on the spreading process, Carboxy-Methyl-Cellulose (CMC) was added to water to increase its viscosity.

Comparison of Computed and Physical Modelling Profiles

To a degree, a computer model can be calibrated to physical modelling data. For the spill model developed in this study, the "fitting" coefficients are:

(i) Manning coefficient - for the physical experiments carried out on the plywood, and,

(ii) a combination of Manning coefficient, initial infiltration and infiltration decay coefficient, for the sod experiments.

Maximum depth and location of the leading edge were used as the primary fitting parameters. However, in the calibration efforts for the various physical model runs, the focus was on obtaining representative behaviour while retaining consistency in the parameters from one run to another. In total, 37 physical model tests were carried out; for a complete description of the results, see Ross and McBean (1986).

As summary comments on the comparisons between the mathematical and physical modelling results, the following are appropriate:

(i) the modelling of the plywood spills was very successful. The modelling of spills on sod was more difficult due to variable infiltration rates. As expected, the Manning coefficient is very difficult to assign. This concern is particularly relevant for grassed areas (for flow between grass blades, the extent to which the grass blades bend, impacts on the frictional resistance). There is even some difficulty in assigning the Manning coefficient for plywood, in part because at low depths of flow, the Manning coefficient is a function of depth. A summary of the results of some experiments is provided in Table 2. Results indicating location of the leading edge, as measured and as calculated for plywood and sod surface covers, are provided in Figures 3 and 4.

(ii) with the sod, and under sloped conditions, the computer model underpredicts the velocity of the leading edge movement. When the surface slope is "sufficiently" large, a different profile results. This occurs when the so-called "normal depth" is smaller than the "critical depth" (i.e. an S2 profile occurs rather than M2 profile. See Henderson (1966) for further details on profile naming conventions).

The mathematical model seems to be capable of reasonably accurately characterizing the excursion of spills of liquids.

Application of Model to Alternative Situations

To explore the mathematical model sensitivities, a series of separate computer runs were carried out. For the first three runs briefly described below, the input parameters to the model were kept constant with the exception of the parameter for which sensitivity was being tested, to allow comparisons between the output. The computer runs, and brief comments on each, are provided below:

(i) the impact of alternative contact angles is depicted in Figure 5. It is apparent that over a considerable range (from 25° to 70°) little change in spill excursion occurs. Specifically, after 25 seconds, the range is from 1.75 m to 2.25 m, only a modest change;

(ii) the impact of changes in density is depicted in Figure 6. Changes in density by itself have minimal impact on spill excursion;

Table 2 Modelling Results of Water - Two-Dimensional Analyses

Run No.	Slope Condition	Surface Condition	Flow Rate(*) $m^3/s.m$	Manning Coefficient (best-fit value)	Infiltration		Maximum Depths (mm)	
					Initial (m/hr)	Decay Coeff. (1/hr)	Measured	Computed
1	flat	plywood	.00046	.01	0	0	9,8,8,10	7
2	flat	plywood	.0012	.005	0	0	10,9,9.5,10	9
3	flat	plywood	.0017	.005	0	0	9,12,11,13	10
4	10° slope	plywood	.0014(**)	.015	0	0	8,10,9	3
5	10° slope	plywood	.0031(**)	.015	0	0	11,10,10	4
6	10° slope	plywood	.0039(**)	.015	0	0	11,11,10	5
7	flat	sod	.00048	.75	1.3	.005	25,25	27
8	flat	sod	.0012	.65	2.5	.005	38,47,37,38	53
9	flat	sod	.0017	.65	2.5	.005	45,41,37,37,33,35	67
10	10° slope	sod	.00096(**)	.05	2.5	.007	25	79
11	10° slope	sod	.0024(**)	.05	2.5	.007	40	177
12	10° slope	sod	.0034(**)	.075	2.5	.007	34	219

Notes - all of the above-indicated results relate to water

- (*) ℓ/min values from the experiments have been translated to $m^3/(sec.m)$. As well, these are flow rates at the location of the spill

- (**) these experiments have flow rates all in one direction, down the slope, as opposed to the experiments on the flat condition which have been presumed to have equal flow in each direction

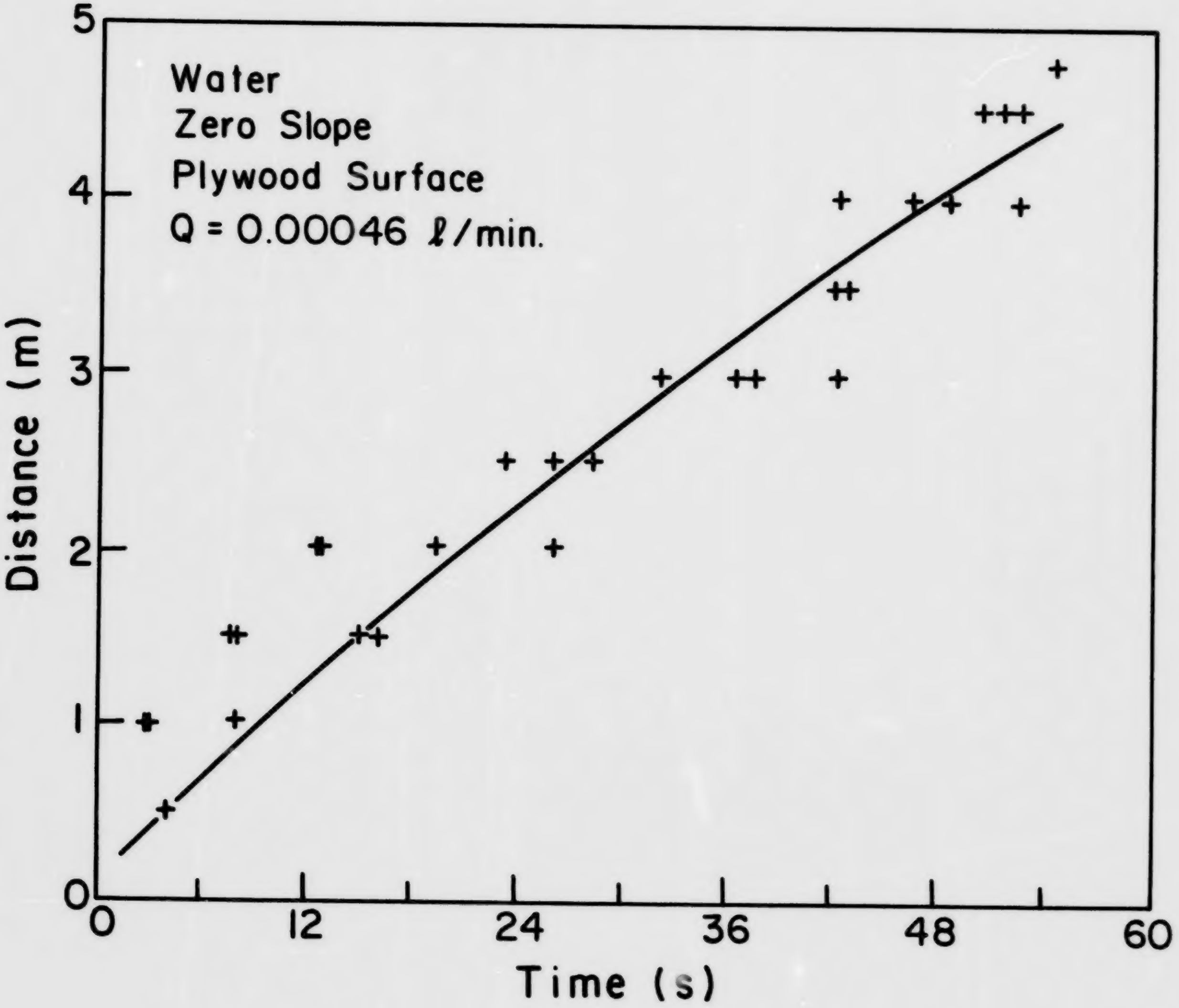

Figure 3 Leading Edge Distance vs. Time, Plywood Surface

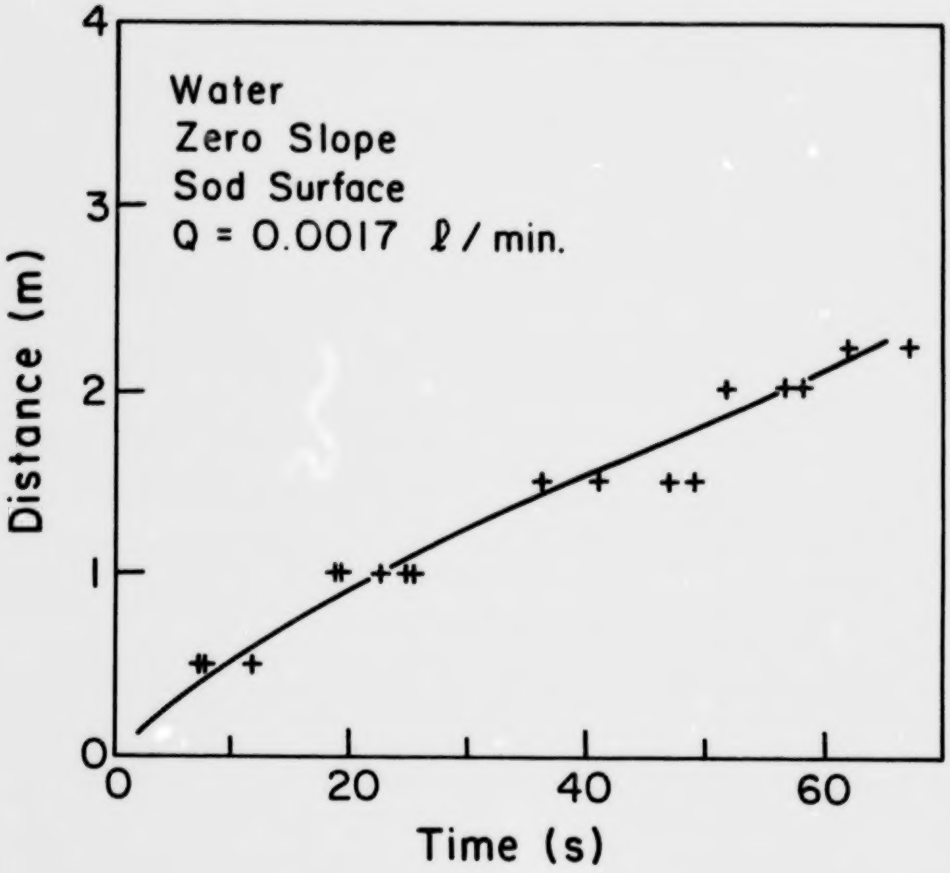

Figure 4 Leading Edge Distance vs. Time, Sod Surface

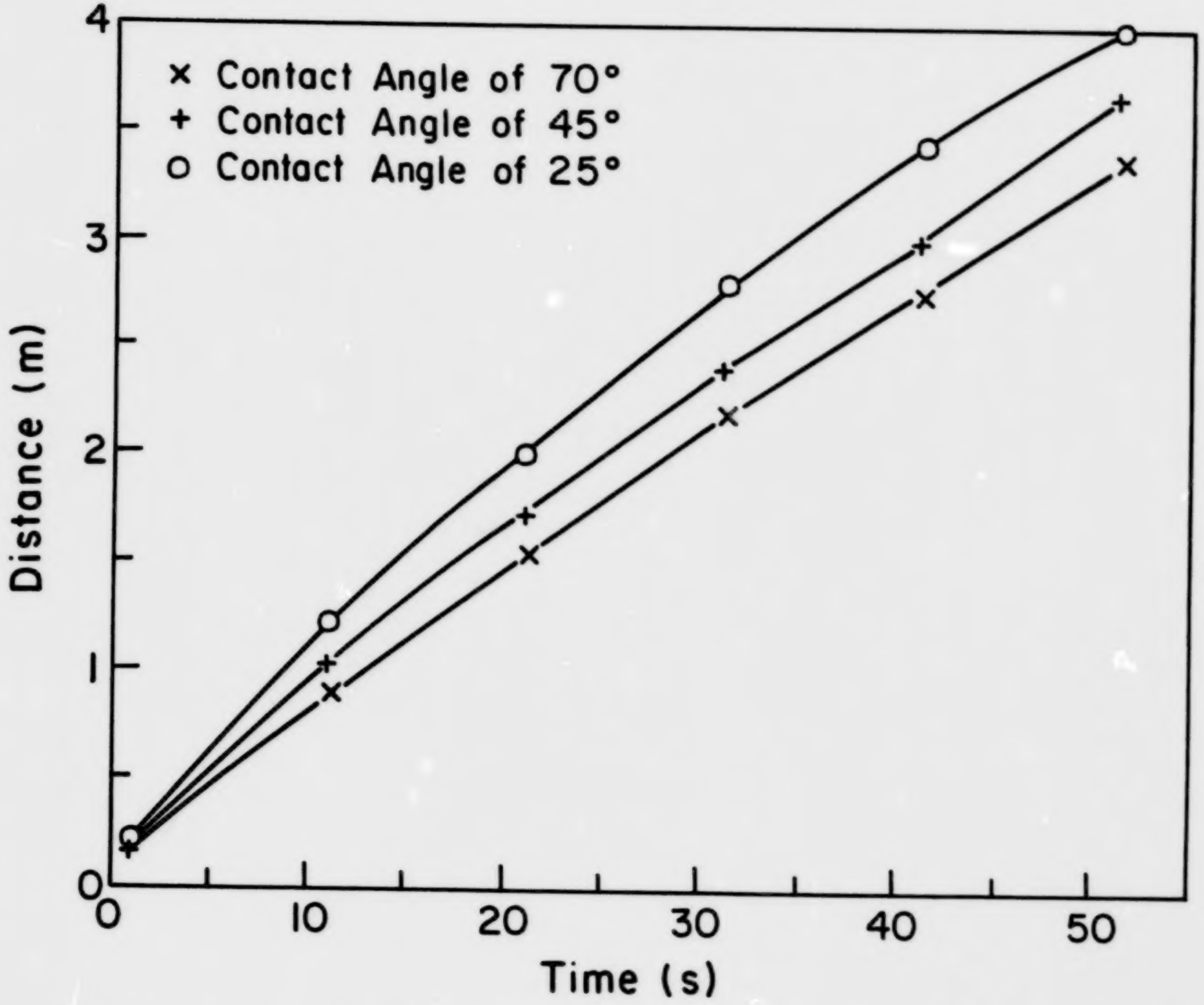

Figure 5 Sensitivity of Spill Excursion to Changes in Contact Angle ($\sigma = .074$, $\rho = 1000$, slope = 0)

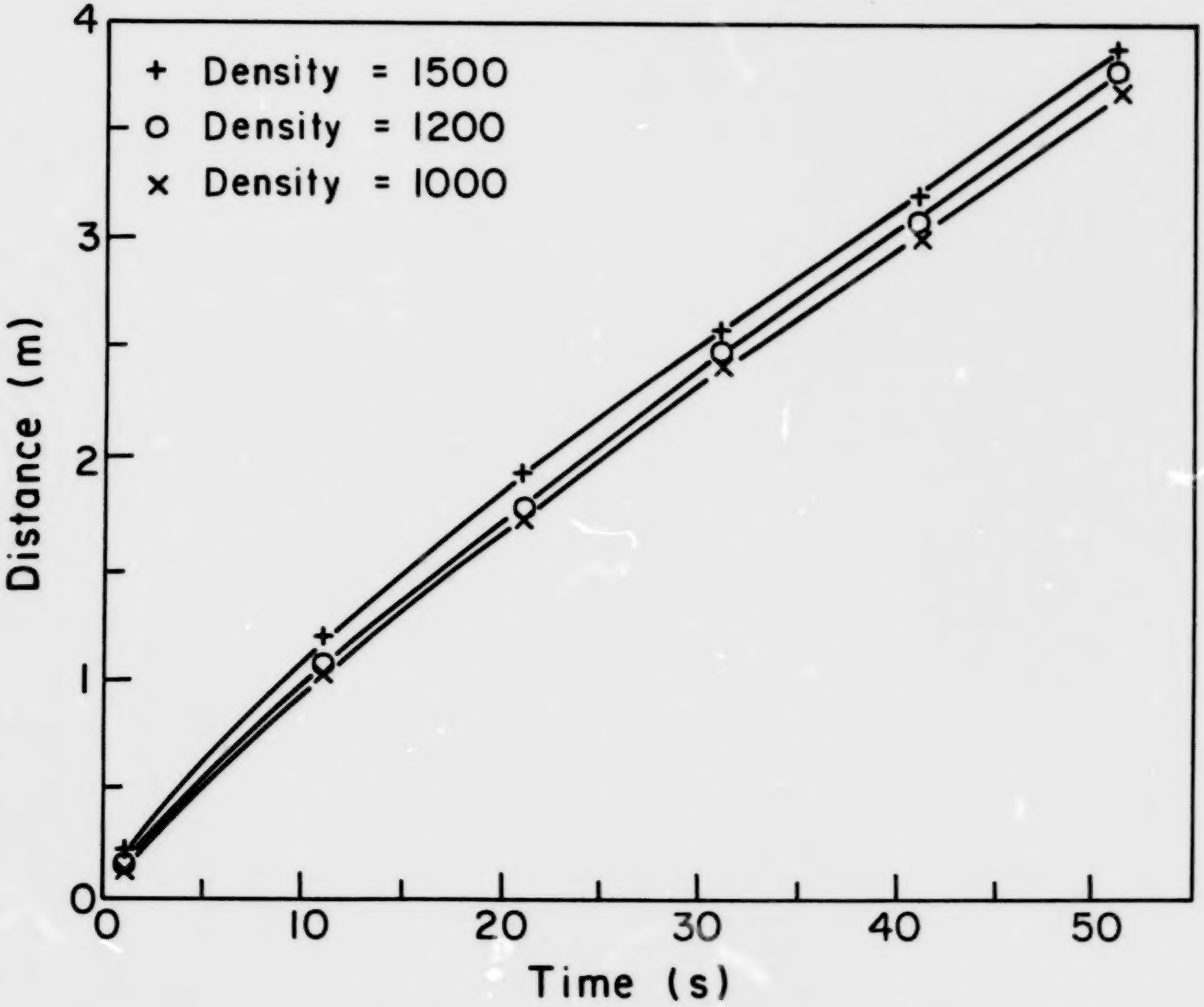

Figure 6 Sensitivity of Spill Excursion to Changes in Density
(σ = .074, α = 45, slope = 0)

(iii) the impact of changes in slope of the solid surface is depicted in Figure 7. The sensitivity to slope is seen to be large and nonlinear (the differential between zero and two degrees is different from the differential between two and four degrees).

As further tests of the model, long-term simulations were undertaken, such as depicted in Figure 8. In the situations where the evaporative flux, infiltrative flux and/or combinations of both, were sufficiently large relative to the liquid spill rate, the spill excursion eventually terminated when the liquid quantity in the spill profile approached zero.

Alternatively, when the infiltration and evaporative flux rates were set to zero, the spill size continues to grow; the rate of curvature of the leading edge distance with time decreases as time increases. However, there is always a small curvature (although the magnitude of the curvature approaches zero) since there is always a sloped profile - surface necessary for the momentum, or forcing function, to make the leading edge continue to migrate away the spill.

The excursion rates are a function of the liquid involved. Depicted in Figure 9 are the excursions of water and kerosene as a function of time, for a three-dimensional spill (on a flat surface). The excursion of water is considerably in excess of that of kerosene.

Data Needs for the Model

The mathematics of the spill model are relatively straightforward. The difficulties with future application of applications of the model will require data, particularly as related to hazardous liquids. Specifically, the needs exist for:

(i) surface tensions and contact angles relating to hazardous liquids; and,

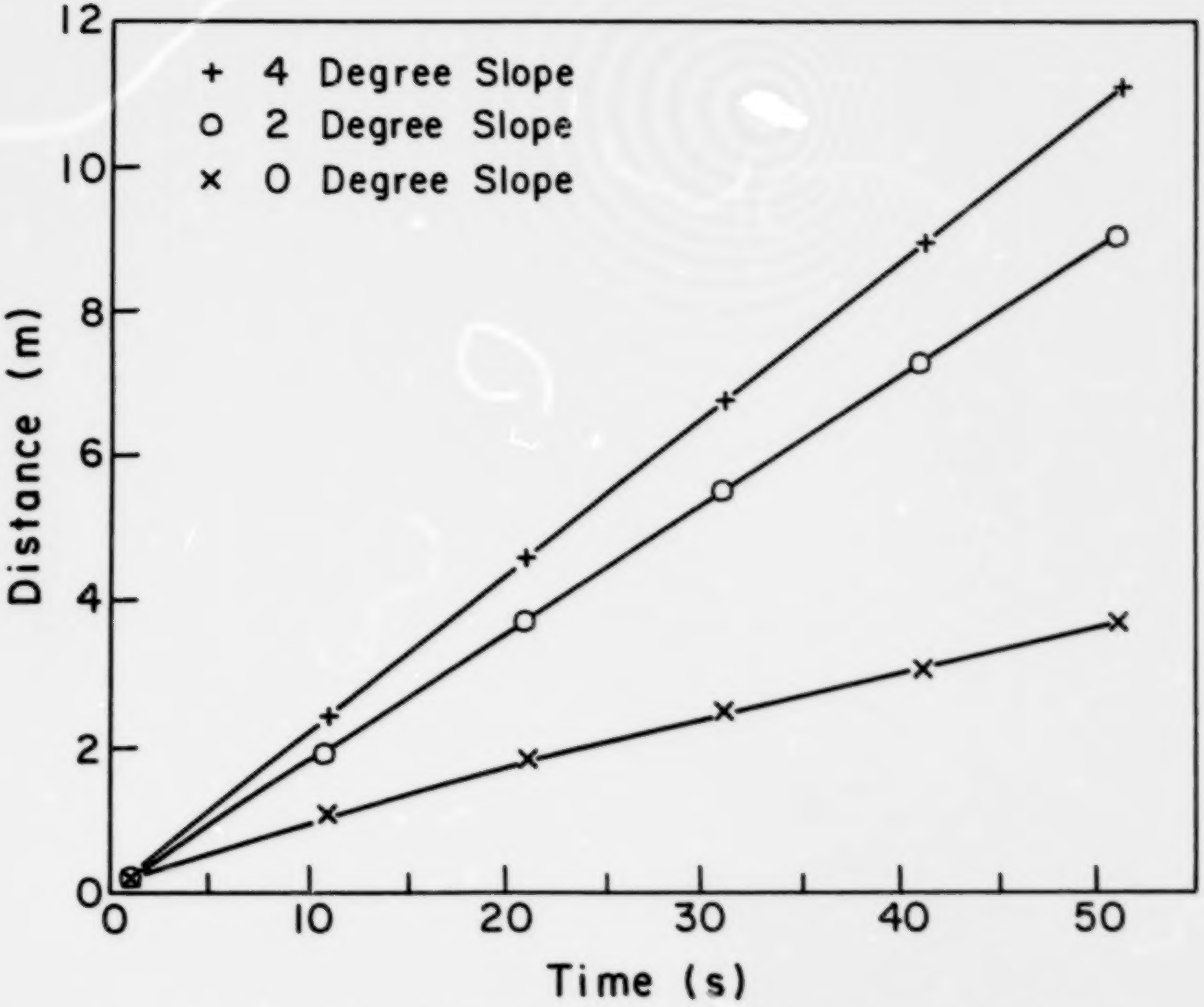

Figure 7 Sensitivity of Spill Excursion to Changes in Slope of Solid Surface (σ = .074, α = 45°, ρ = 1000)

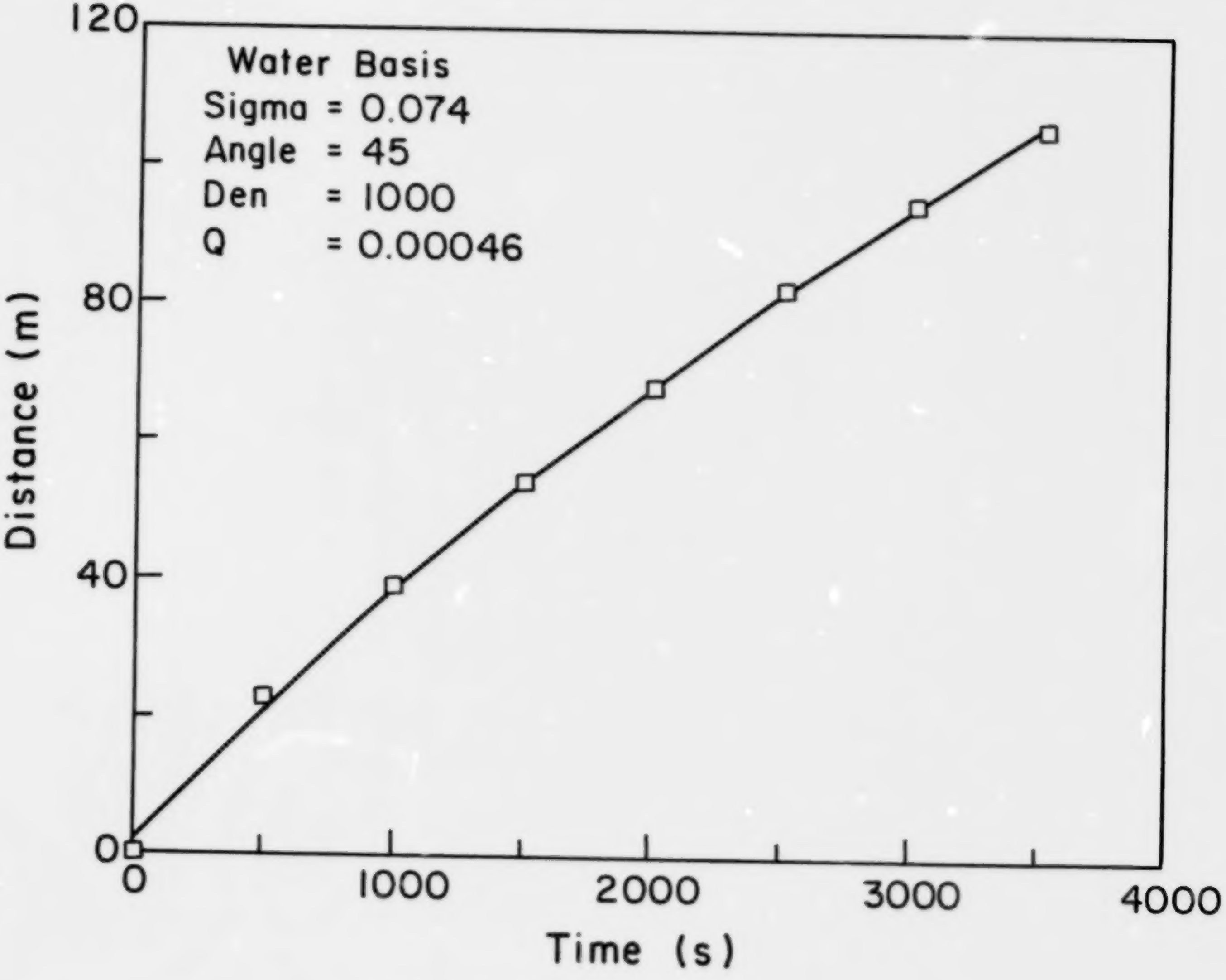

Figure 8 2D Spill Model Long Run

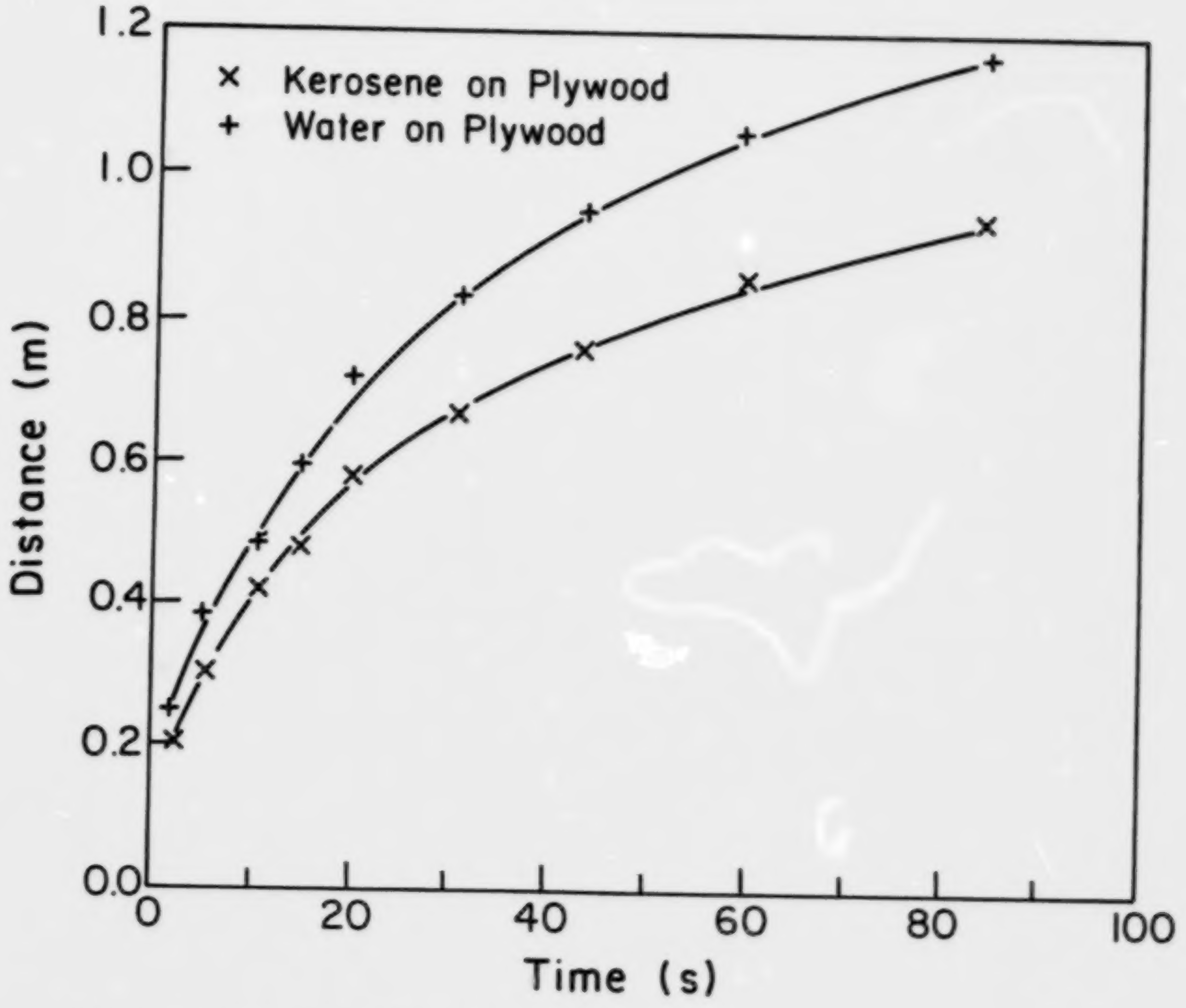

Figure 9 Excursions of Kerosene and Water on Plywood, on a Flat Surface

(ii) friction resistance coefficients for liquids other than water. Preliminary aspects of this problem are provided in McBean and Belore (1986) but much work remains to be done.

CONCLUSIONS

A simple two- and three-dimensional model applicable to the most common spill situations was described. The validity of the predictions of the model was demonstrated by application to a variety of laboratory experiments, with good results.

Sensitivity testing showed that differences in density and contact angle were of lesser importance in forecasting spill excursions than are variations in the slope of the solid surface. Additional, fundamental data characterizing friction coefficients, contact angles etc., as needed for model application are important for future utility of the model.

ACKNOWLEDGEMENTS

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A RAPID ASSESSMENT MODEL FOR SPILLS ON SOIL OF OILY FLUIDS THAT ARE IMMISCIBLE WITH WATER

Douglas E. Metcalfe and George Zukovs

CANVIRO CONSULTANTS, A Division of
CH2M HILL Engineering Ltd.
Kitchener, Ontario, CANADA

ABSTRACT

A subsurface transport model has been developed for spills on soil of oily fluids that are immiscible with water. This rapid assessment tool has been developed for spill respondents who are not necessarily contaminant transport specialists for use in evaluating the environmental severity and impacts of spills and determining the need for emergency actions. As such, model inputs are limited to the key data requirements, with guidelines provided on the selection of those data. The model equations are presented in nomogram format, allowing the migration distances and times of the contaminant fluid to be graphically obtained.

The model accounts for the downward migration of contaminant fluids and the behaviour of these fluids at the water table, for both fluids that are less dense and more dense than water. The nomograms describing these phenomena are based on Darcian flow concepts and published experimental work. Step-by-step instructions are provided in a worksheet format on the use of the nomograms for obtaining estimates of depths of penetration at specified times, the time of penetration to the water table, the extent of potential contamination at the water table, and the ultimate subsurface configuration of the contaminant fluid.

INTRODUCTION

Environment Canada initiated the Environmental and Technical Information for Problem Spills (EnviroTIPS) series of manuals (Environment Canada, 1983) in 1981 to provide comprehensive information on chemicals that are frequently spilled in Canada. The manuals are intended to be used by persons assessing the impacts of spills on the environment, developing spill countermeasures and formulating spill contingency plans.

To date, manuals for 50 chemicals are complete, and a polychlorinated biphenyls (PCBs) EnviroTIPS manual is underway (CANVIRO CONSULTANTS, 1986). The rapid assessment model for subsurface transport described in this paper is derived from the PCB EnviroTIPS manual. The PCB subsurface transport model has been generalized to address the family of oily fluids that are immiscible with water, including:

- petroleum products, such as fuels, heating oils, motor oils and cutting oils, and

- other organic fluids derived from natural substances (e.g. benzene, toluene) and man-made organic fluids (e.g. aliphatic chlorohydrocarbons, PCBs) of similar viscosity to the above-mentioned petroleum products.

The model addresses the fluid (immiscible with water) phase only; any dissolved (aqueous) phase of the contaminant is not considered. In the short term, the bulk of the contaminant will exist in the fluid phase, and the fluid phase is the source of all dissolved contaminants in the groundwater. Papers on the remediation of hydrocarbon spill sites (eg. Yaniga, 1982; Blake and Lewis, 1983) are unanimous in stating that the first clean-up step is to remove the contaminant source and any free product, to avoid further contamination of groundwater resources. The rapid assessment model can be used to estimate the extent and location of contaminated soil and any free product on top of the water table.

MODEL OBJECTIVES AND APPROACH

The primary objective of the Subsurface Transport Rapid Assessment Model (STRAM) is to provide a means for spill response personnel to make first-cut estimates of the extent of soil and groundwater contamination due to spills of oily fluids immiscible with water. Specifically, the model is designed to quickly estimate the following:

- the current depth of penetration of the spilled fluids;
- the potential for the spilled fluids to reach the water table;
- the time at which any spilled fluids will reach the water table; and
- the ultimate subsurface configuration of the spilled fluids.

The STRAM is intended for spill response personnel who are not necessarily contaminant transport specialists or hydrogeologists. Additionally, time and resource limitations are anticipated under spill response conditions. As such, it was necessary to incorporate a number of features in the model to allow non-specialists to quickly perform the types of first-cut estimates of contamination described above. These features include the following model simplifications and aids to make the model "user-friendly" and conducive to its rapid assessment role:

- the STRAM was streamlined to provide only the key measures of fluid migration described above;
- the input requirements were limited to only those data types for which values could be reasonably obtained or estimated under spill response conditions;
- guidelines are provided for estimating values for all input requirements;
- the model equations are presented in nomogram format, to allow for the graphical calculation of all measures of fluid migration; and

- the methodology for using the nomograms to assess soil and groundwater contamination is provided in a worksheet format.

The intent was to incorporate only conservative assumptions in the model. However, it was not possible to account for every conceivable situation without unduly complicating the presentation of the model. Instead, notes are included to explain the potential situations under which the STRAM will not provide conservative estimates of the extent of soil and groundwater contamination.

TECHNICAL BACKGROUND

The subsurface migration of spilled oils and petroleum products has been extensively studied, with notable works including Schwille (1967, 1975), Dietz (1971), API (1972) and Van Dam (1967). Schwille (1984) extends many of the concepts described in these papers to anthropogenic organic chemicals that are immiscible with water. The STRAM is largely based on the above-mentioned works and Freeze and Cherry (1979). A brief description of the processes causing and affecting the subsurface transport of oily fluids that are immiscible with water is provided below.

The infiltration and downward transport of fluids immiscible with water through the soil involve multi-phase phenomena. The phases of concern are the fluid, water, soil and the soil gases. Due to the complexities of these multi-phase phenomena, simplifications in the representations of fluid, soil and groundwater conditions are required. Figure 1 illustrates the idealized representation of the subsurface movement of fluids immiscible with water that was assumed for the model. As shown in Stage 1 of Figure 1, the spill is assumed to result in a spill pool on ground surface. The spilled fluids fill the pores at the soil surface and begin to penetrate downward. During the spill event, and until such time as any spill pool formed as a result of the spill event is dissipated due to evaporation, soil penetration and/or clean-up activities, the fluids penetrate the soil according to Darcy's Law as a saturated slug. This is shown as Stage 2 in Figure 1.

After the spill pool is dissipated (Stage 3, Figure 1), the spilled fluids continue to migrate downward as a saturated slug, but leave behind a constant residual amount within the soil pores (Stage 4, Figure 1). This downward movement continues until the slug is exhausted as residual fluid. The depth at which this occurs is the ultimate penetration depth, d_u (m), which is shown as Stage 5 in Figure 1.

The presence of a water table can, however, alter this pattern of subsurface migration. If a depth of unsaturated soil greater than the depth to the water table is required to exhaust the spilled fluid as residual fluid, then the spilled fluid will reach the water table. Fluids that are immiscible with and less dense than water, such as mineral oils, will spread within the capillary fringe in the shape of a pancake, as shown in Figure 2. Fluids that are immiscible with and more dense than water, such as PCBs, will tend to sink below the water table and continue to migrate in a downward direction, as shown in Figure 3. Similarly, an impermeable layer can act as a barrier to downward flow. As shown in Figure 3, fluids reaching such a barrier tend to spread on top of the impermeable barrier.

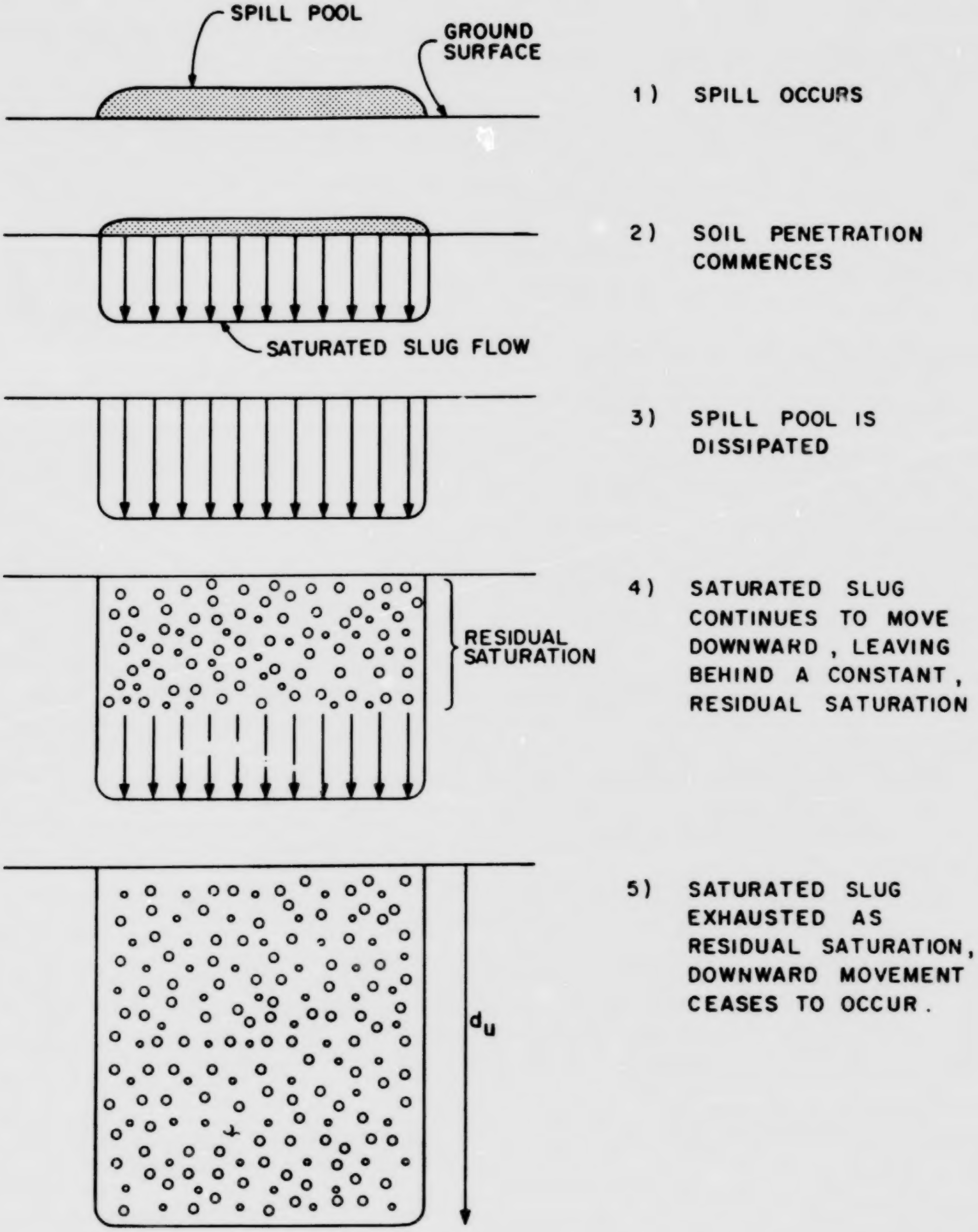

SPILL POOL
GROUND SURFACE
1) SPILL OCCURS
2) SOIL PENETRATION COMMENCES
SATURATED SLUG FLOW
3) SPILL POOL IS DISSIPATED
RESIDUAL SATURATION
4) SATURATED SLUG CONTINUES TO MOVE DOWNWARD, LEAVING BEHIND A CONSTANT, RESIDUAL SATURATION
d_u
5) SATURATED SLUG EXHAUSTED AS RESIDUAL SATURATION, DOWNWARD MOVEMENT CEASES TO OCCUR.

FIGURE 1 – IDEALIZED REPRESENTATION OF THE SUBSURFACE PENETRATION AND MOVEMENT OF FLUIDS IMMISCIBLE WITH WATER

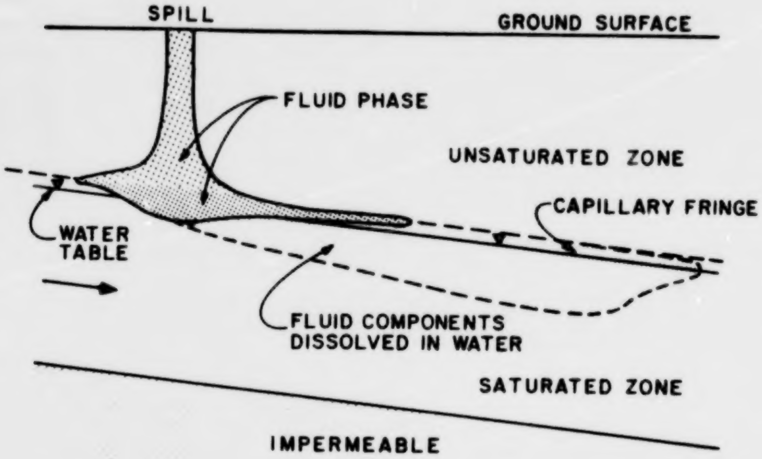

SPILL
GROUND SURFACE
FLUID PHASE
UNSATURATED ZONE
CAPILLARY FRINGE
WATER TABLE
FLUID COMPONENTS DISSOLVED IN WATER
SATURATED ZONE
IMPERMEABLE

FIGURE 2 — SUBSURFACE TRANSPORT OF FLUIDS IMMISCIBLE WITH AND LESS DENSE THAN WATER

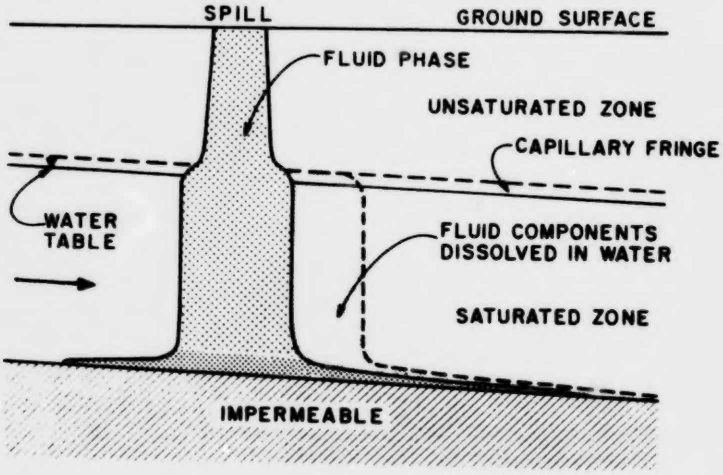

SPILL
GROUND SURFACE
FLUID PHASE
UNSATURATED ZONE
CAPILLARY FRINGE
WATER TABLE
FLUID COMPONENTS DISSOLVED IN WATER
SATURATED ZONE
IMPERMEABLE

FIGURE 3 — SUBSURFACE TRANSPORT OF FLUIDS IMMISCIBLE WITH AND MORE DENSE THAN WATER

Figures 2 and 3 also show the potential for the oily fluids to dissolve into and move with the groundwater. As previously stated, the dissolved phase of a fluid immiscible with water represents only a small fraction of the total volume of spilled fluid in the short term. The formation and migration of the dissolved phase is therefore not considered in the STRAM. Donigian et al (1983) present a rapid assessment model for potential groundwater contamination due to dissolved contaminants.

The major assumptions used in the STRAM are as follows:

- soils are homogeneous and isotropic with respect to soil permeability.
- the downward movement of the leading edge of contaminant fluids can be characterized as saturated Darcian flow, and thus, no reductions are required in the value of soil permeability for less-than-saturated conditions.
- vertical migration in the unsaturated zone is due to gravitational forces only.
- no lateral migration occurs in the unsaturated zone.
- no dissolution or volatilization of contaminants occur from the fluid phase.
- fluids penetrate the soil surface uniformly across the spill area.
- soil contains water at its field capacity from ground surface to the water table.
- water table elevation does not fluctuate.

INFORMATION REQUIRED TO ASSESS THE SUBSURFACE TRANSPORT OF OILY FLUIDS IMMISCIBLE WITH WATER

The data types required to use the STRAM nomograms are listed in the following subsections, and guidelines are provided for selecting values for each of the data types.

Fluid Absolute Viscosity and Density - Absolute viscosity, μ (Pa.sec) and fluid density, ρ (kg/m^3), data as a function of temperature should be obtained for all fluid types that are used or stored. This fluid property data should be appended to the STRAM, so that it will be readily available in the event that a spill situation arises. Lange's Handbook of Chemistry (Dean, 1973), the CRC Handbook of Chemistry and Physics (Weast, 1974) and Reid et al (1977) are sources of absolute viscosity and fluid density data for many organic fluids, and the latter reference provides equations for converting fluid property data to different temperatures. Additionally, chemical suppliers may be able to provide such information.

Ideally, the temperature used in selecting values for absolute viscosity and fluid density should be the average soil temperature between land surface and the water table at the spill site. An estimate of the ambient air temperature can, however, be used in place of soil temperature.

Fluid Kinematic Viscosity - Kinematic viscosity, ν (m^2/sec), is calculated from the values of absolute viscosity and fluid density:

$$\nu = \mu/\rho \qquad (1)$$

where μ (Pa.sec) is absolute viscosity and ρ (kg/m^3) is fluid density.

Soil Type - Where possible, soil type should be determined based on information provided by persons familiar with the hydrogeologic conditions near the spill site (eg. local well drilling firms, hydrogeologic or geotechnical engineers, government agencies). Categorize the soil type as one of the following:

- Gravel
- Clean sand
- Silty sand
- Silt
- Glacial till
- Clay

↓ Less permeable

The soil type should be representative of the soils existing between land surface and the water table. For layered soil systems where more than one soil type occurs between land surface and the water table, use of the least permeable soil type will yield the most likely penetration times to the water table, whereas use of the most permeable soil type will yield the most conservative penetration times.

Soil Permeability - Figure 4 shows the relationship between soil type and soil permeability, k (m^2) (Freeze and Cherry, 1979). For convenience, all other soil properties used in this section are presented in terms of soil permeability. Note that the value of soil permeability can range over several orders of magnitude for a given soil type. Thus, it may be necessary to evaluate subsurface transport for a range of soil permeability values. In many instances the soil hydraulic conductivity for water, K_w (m/sec), will be available for the spill site, and therefore, the relationship between k and K_w is provided in Figure 4 to aid in establishing the value for soil permeability.

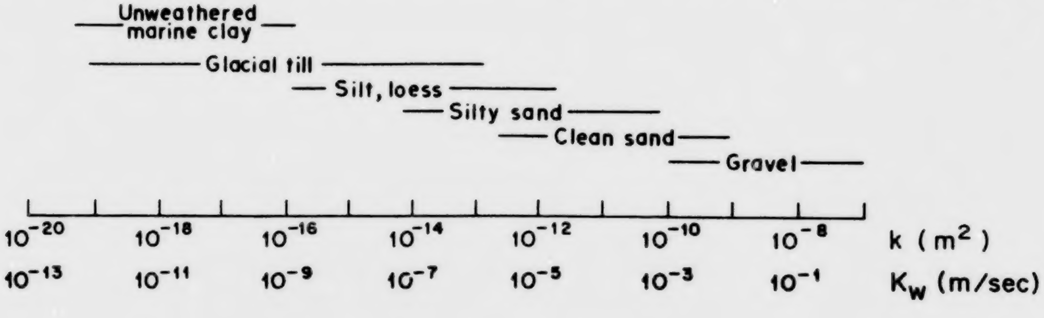


FIGURE 4 — PERMEABILITY AS A FUNCTION OF SOIL TYPE

Water Table Depth - Knowledge of the water table depth, d_w (m), at the spill site is important in assessing the potential for the fluids to reach the water table and result in contamination of the local groundwater resources. As with soil type, local well drilling firms and/or hydrogeologic/geotechnical engineering firms and/or government agencies that are familiar with hydrogeologic conditions in the vicinity of the spill site should be contacted to aid in determining water table depth.

Time History of Fluid Spill - At a minimum, the elapsed time since the spill event commenced, t_c (min), should be approximately known. Any additional knowledge regarding the nature of the spill is of value in assessing the subsurface transport of the spilled fluids.

Volume of Fluid Spilled and Volumetric Loading on Soil Surface - The volume of fluids spilled, V_s (m^3), can be calculated based on the difference in volumes contained in the ruptured container before (V_o) and (V_f) after the spill event, less the volumes of fluid recovered from the spill pool during clean-up operations (V_r):

$$V_s = V_o - V_f - V_r \qquad (2)$$

The volumetric loading of spilled fluids on the soil surface, h (m), is calculated as follows:

$$h = V_s / A_s \qquad (3)$$

where A_s (m^2) is the area of the spill pool, which can be approximately measured at the spill site. The volumetric loading is equivalent to the initial spill pool thickness in essentially instantaneous spill events, where the entire volume of fluids is spilled prior to significant permeation of the fluids into the soil.

SUBSURFACE TRANSPORT NOMOGRAMS FOR OILY FLUIDS IMMISCIBLE WITH WATER

The following subsections describe the three nomograms used in the STRAM.

Figure 5: Penetration Time Versus Penetration Depth - The relationship between penetration time, t (min), and penetration depth, d (m), is shown in Figure 5, based on the Darcy flux for saturated slug flow, v (m/sec):

$$d = 60vt/n \qquad (4)$$

$$v = -\frac{k\rho g i}{\mu} = \frac{kg}{\nu} \qquad (5)$$

where k (m^2) is soil permeability, ρ (kg/m^3) is fluid density, μ (Pa.sec) is absolute viscosity, g (9.81 m/sec^2) is acceleration due to gravity, ν (m^2/sec) is kinematic viscosity, n () is effective porosity, and the fluid gradient, i (), is equal to -1.

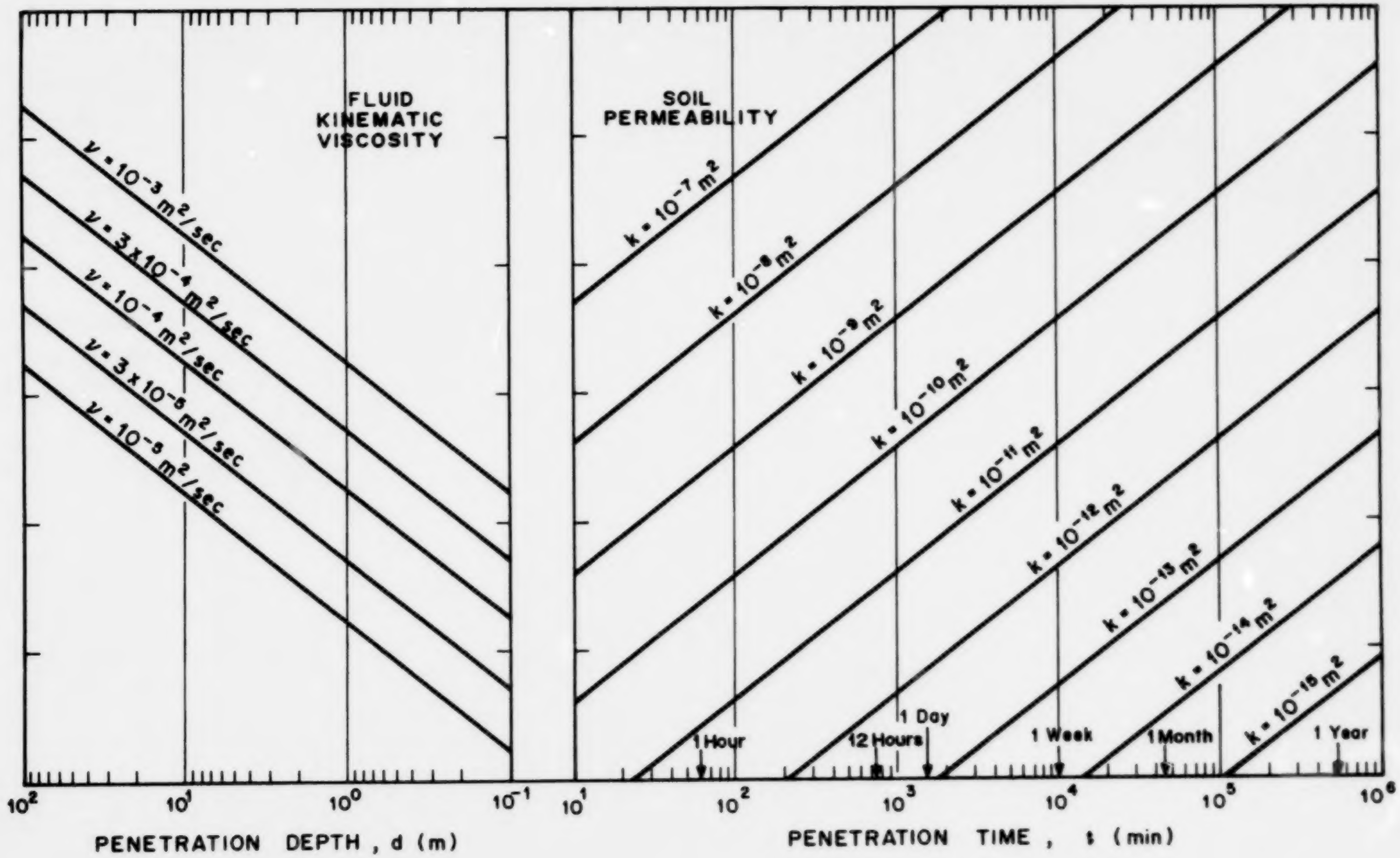


FIGURE 5 – PENETRATION TIME VERSUS PENETRATION DEPTH

Table 1 shows representative values for porosity and field capacity as functions of soil permeability (Todd, 1980; Freeze and Cherry, 1979; Bouwer, 1978). Effective porosity, which is also shown in Table 1, is calculated by subtracting field capacity from porosity. The use of a particular value for soil permeability in Figure 5 implies the use of the corresponding value for effective porosity in Table 1.

Penetration depth in Figure 5 can be the ultimate penetration depth, depth to the water table, or any other depth of penetration of interest. For example, the following operations are performed to calculate current penetration depth:

1) Estimate the time in minutes that has elapsed since the occurrence of the spill, and enter the nomogram at that point on the "Penetration Time" scale.

2) Move vertically upward to the line for the appropriate value of soil permeability, k (m^2).

3) Move horizontally to the left to the line for the appropriate value of fluid kinematic viscosity, ν (m^2/sec).

4) Move vertically downward to obtain the value for penetration depth, d (m).

Alternatively, Figure 5 can be used in reverse order to calculate the time at which a given penetration depth (eg. depth to water table) will occur.

The penetration time versus penetration depth nomogram is particularly illustrative of the large impacts that uncertainties in soil permeability have on predicted fluid penetration depths and times.

TABLE 1 GENERALIZED RELATIONSHIP BETWEEN SOIL PERMEABILITY AND EFFECTIVE POROSITY

Permeability (m^2)	Porosity ( )	Field Capacity ( )	Effective Porosity ( )
10^{-7}	0.28	0.05	0.23
10^{-8}	0.31	0.05	0.26
10^{-9}	0.34	0.05	0.29
10^{-10}	0.36	0.07	0.29
10^{-11}	0.38	0.10	0.28
10^{-12}	0.40	0.16	0.24
10^{-13}	0.42	0.22	0.20
10^{-14}	0.44	0.28	0.16
10^{-15}	0.46	0.34	0.12
10^{-16}	0.50	0.40	0.10

Figure 6: Ultimate Penetration Depth Versus Volumetric Loading - Ultimate penetration depth, d_u (m), is a function of volumetric loading, h (m), and residual fluid content, U_o (m^3/m^3):

$$d_u = h/U_o \tag{6}$$

Under spill response conditions, it is doubtful that a value for residual fluid content will be readily available. Residual fluid content is, however, related to soil permeability (Schwille, 1975), which must be estimated to assess subsurface transport. Table 2 was developed from Schwille's generalized relationship between soil permeability and residual fluid content. Schwille states the relationship is valid for light and medium oils of low viscosity, such as extra-light and light fuel oil, diesel fuel and kerosene. Schwille (1984) later states that similar values were found in laboratory experiments for an organic chemical, and that on the basis of theoretical considerations the available information on the subsurface transport of petroleum products can generally be applied to organic chemicals.

While there are large uncertainties in soil permeability values from Figure 4, it must be noted that the entire range of residual fluid content values is approximately one order of magnitude. Given the lack of residual fluid content data that is anticipated for virtually all spill sites and in the interest of reducing the number of model input requirements, soil permeability was used in Figure 6 in place of residual fluid content based on Table 2. Equation 6 can be used for spill sites for which residual fluid content data are available, or for which the soil permeability versus residual fluid content relationship in Table 2 is not suitable.

TABLE 2 GENERALIZED RELATIONSHIP BETWEEN SOIL PERMEABILITY AND RESIDUAL FLUID CONTENT

$k(m^2)$	$U_o(\ )$	$k(m^2)$	$U_o(\ )$
$\geq 10^{-8}$	3.9×10^{-3}	10^{-11}	1.9×10^{-2}
10^{-9}	6.3×10^{-3}	10^{-12}	3.2×10^{-2}
10^{-10}	1.1×10^{-2}	$\leq 10^{-13}$	4.5×10^{-2}

Figure 7: Contamination at the Water Table Surface Due to Spills of Fluids Less Dense than Water - As previously stated, fluids can cause contamination at/below the water table in the event that the ultimate penetration depth, d_u, is greater than the depth to the water table, d_w. For fluids that are immiscible with and less dense than water, such as mineral oils, the fluids that reach the water table tend to float on top of the water table in the shape of a pancake, as shown in Figure 2.

The area at the water table surface that is ultimately contaminated with spilled fluids, A_w (m^2), is a function of the volume of spilled fluids penetrating to the water table, V_w (m^3), and the final layer or "pancake" thickness, D_o (m^3/m^2):

$$A_w = V_w / D_o \tag{7}$$

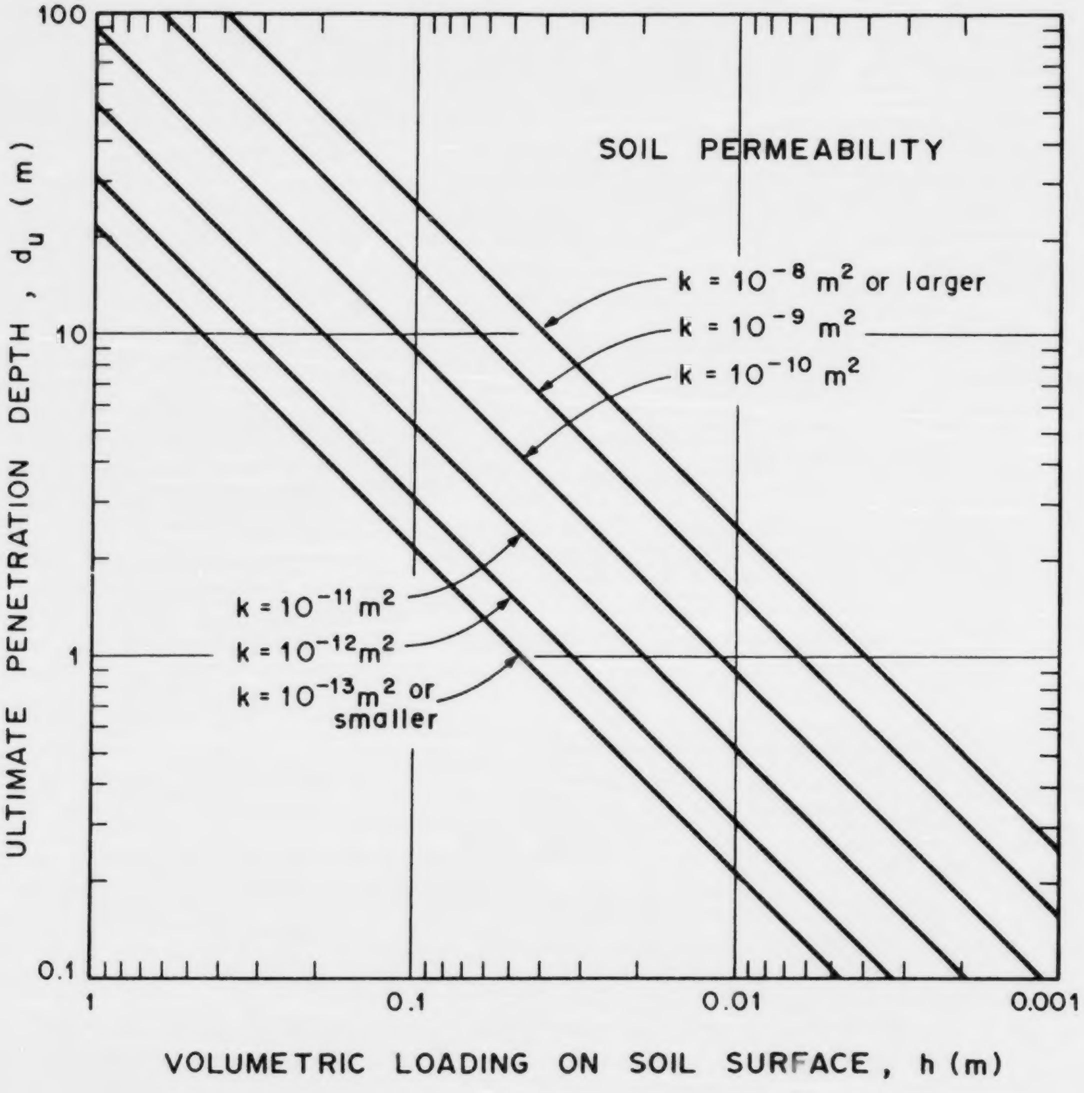


FIGURE 6 - ULTIMATE PENETRATION DEPTH VERSUS VOLUMETRIC LOADING

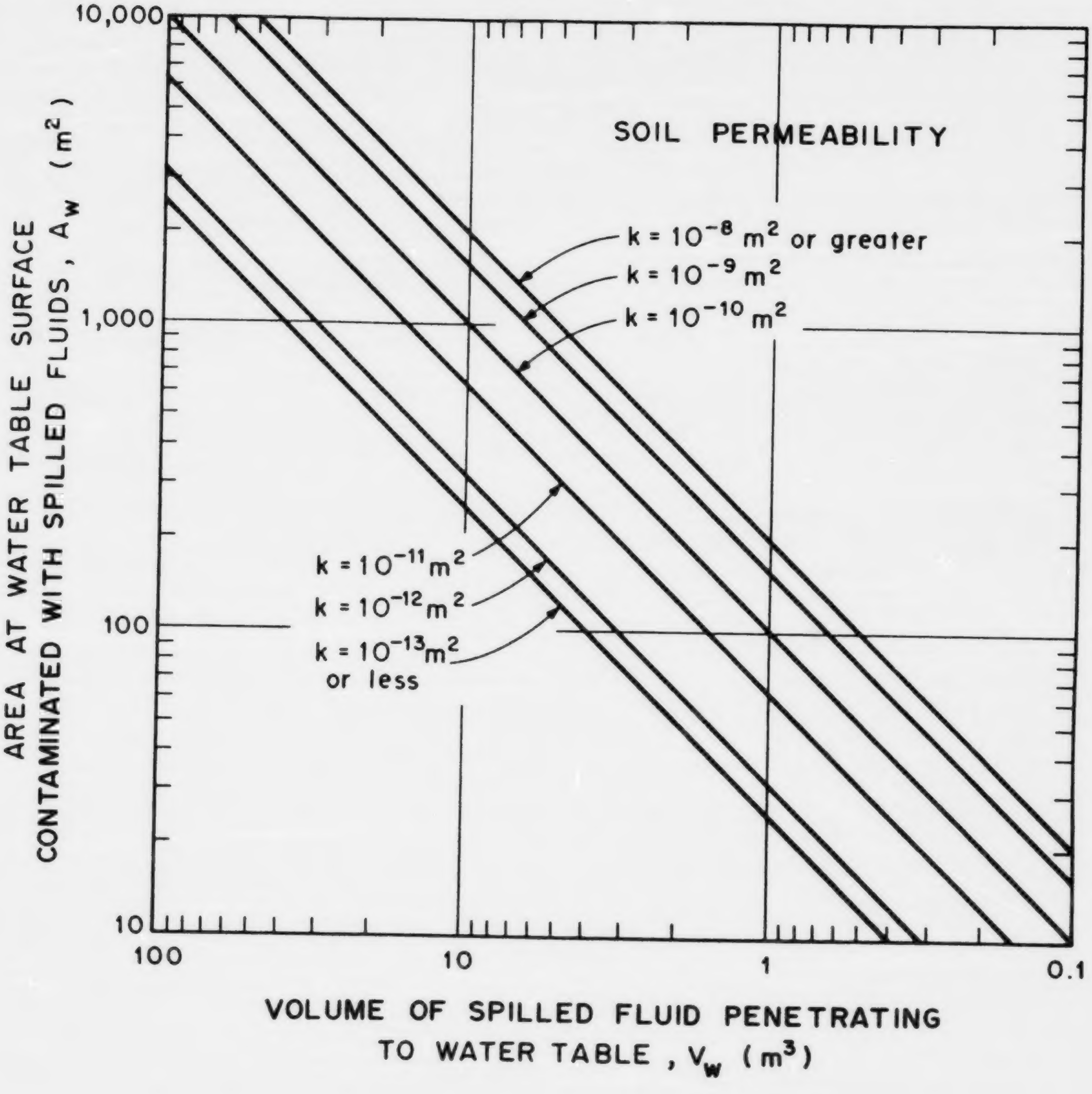


FIGURE 7 - CONTAMINATION AT THE WATER TABLE SURFACE DUE TO SPILLS OF FLUIDS LESS DENSE THAN WATER

where the volume of oily fluids reaching the water table is calculated as follows:

$$V_w = V_s \, (d_u - d_w) \, / \, d_u \qquad (8)$$

and the remaining terms are as previously defined.

As with residual fluid content, it is unlikely that a value for final layer thickness will be available for the soils at a spill site. Schwille (1975) provides a generalized relationship between final layer thickness and soil permeability, and this relationship was used as the basis for Table 3. Figure 7 was therefore developed in a manner similar to that used for Figure 6, with soil permeability used in place of final layer thickness in Figure 7 based on Table 3.

TABLE 3 GENERALIZED RELATIONSHIP BETWEEN SOIL PERMEABILITY AND FINAL LAYER THICKNESS

$k(m^2)$	$D_o(m)$	$k(m^2)$	$D_o(m)$
$\geq 10^{-8}$	5.0×10^{-3}	10^{-11}	1.6×10^{-2}
10^{-9}	6.3×10^{-3}	10^{-12}	3.2×10^{-2}
10^{-10}	9.8×10^{-3}	$\leq 10^{-13}$	4.0×10^{-2}

APPLICATION OF NOMOGRAMS TO EVALUATING SUBSURFACE TRANSPORT OF OILY FLUIDS IMMISCIBLE WITH WATER

The worksheet provided in Figure 8 is used to evaluate the subsurface transport of oily fluids immiscible with water. Figure 8 shows the steps required for evaluating subsurface transport, the parameters that are quantified in those steps and any associated data needs or calculations. Additional instructions for completing the worksheet are provided below:

Steps 1, 2 and 3: Estimate Input Data

Refer to required information section when estimating the input data.

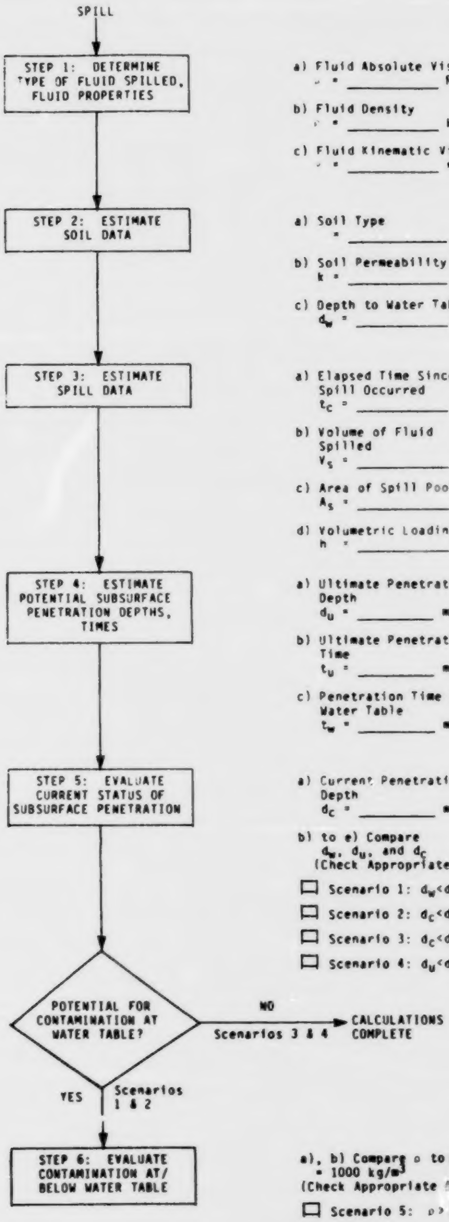
Step 4: Estimate Potential Subsurface Penetration Depths and Times

a) Using Figure 6, estimate ultimate penetration depth, d_u, given h and k.

b) Using Figure 5, estimate ultimate penetration time, t_u, given d_u, ν and k.

c) Using Figure 5, estimate penetration time to water table, t_w, given d_w, ν and k.

Step 5: Evaluate Current Status of the Subsurface Penetration of the Spilled Fluids


SPILL
STEP 1: DETERMINE TYPE OF FLUID SPILLED, FLUID PROPERTIES
STEP 2: ESTIMATE SOIL DATA
STEP 3: ESTIMATE SPILL DATA
STEP 4: ESTIMATE POTENTIAL SUBSURFACE PENETRATION DEPTHS, TIMES
STEP 5: EVALUATE CURRENT STATUS OF SUBSURFACE PENETRATION
POTENTIAL FOR CONTAMINATION AT WATER TABLE?
NO
Scenarios 3 & 4
CALCULATIONS COMPLETE
YES
Scenarios 1 & 2
STEP 6: EVALUATE CONTAMINATION AT/BELOW WATER TABLE

STEPS FOR EVALUATION OF SUBSURFACE TRANSPORT	PARAMETERS QUANTIFIED	DATA NEEDS, HOW/WHERE TO OBTAIN DATA	CALCULATIONS PERFORMED, FIGURES USED
STEP 1: DETERMINE TYPE OF FLUID SPILLED, FLUID PROPERTIES	a) Fluid Absolute Viscosity μ = ________ Pa.sec	Ambient Temperature	
	b) Fluid Density ρ = ________ kg/m^3	Ambient Temperature	
	c) Fluid Kinematic Viscosity ν = ________ m^2/sec	μ,ρ	$\nu = \mu/\rho$
STEP 2: ESTIMATE SOIL DATA	a) Soil Type = ________	Estimate	
	b) Soil Permeability k = ________ m^2	Soil Type	Figure 4
	c) Depth to Water Table d_w = ________ m	Estimate	
STEP 3: ESTIMATE SPILL DATA	a) Elapsed Time Since Spill Occurred t_c = ________ min	Estimate	
	b) Volume of Fluid Spilled V_s = ________ m^3	Estimate	
	c) Area of Spill Pool A_s = ________ m^2	Measure	
	d) Volumetric Loading h = ________ m	V_s, A_s	$h = V_s/A_s$
STEP 4: ESTIMATE POTENTIAL SUBSURFACE PENETRATION DEPTHS, TIMES	a) Ultimate Penetration Depth d_u = ________ m	h, k	Figure 6
	b) Ultimate Penetration Time t_u = ________ min	d_u, ν, k	Figure 5
	c) Penetration Time to Water Table t_w = ________ min	d_w, ν, k	Figure 5
STEP 5: EVALUATE CURRENT STATUS OF SUBSURFACE PENETRATION	a) Current Penetration Depth d_c = ________ m	t_c, k, ν	Figure 5
	b) to e) Compare d_w, d_u, and d_c (Check Appropriate Box) ☐ Scenario 1: $d_w<d_u,d_c$ ☐ Scenario 2: $d_c<d_w<d_u$ ☐ Scenario 3: $d_c<d_u<d_w$ ☐ Scenario 4: $d_u<d_c,d_w$	d_w, d_u, d_c	
STEP 6: EVALUATE CONTAMINATION AT/BELOW WATER TABLE	a), b) Compare ρ to ρ_w = 1000 kg/m^3 (Check Appropriate Box) ☐ Scenario 5: $\rho > \rho_w$ ☐ Scenario 6: $\rho < \rho_w$	ρ, ρ_w	
	For Scenario 6: i) Volume of Spilled Fluid Reaching Water Table V_w = ________ m^3	V_s, d_u, d_w	$V_w = V_s(d_u-d_w)/d_u$
	ii) Area of Contamination Ontop of Water Table A_w = ________ m^2	V_w, k	Figure 7

FIGURE 8 — WORKSHEET FOR ASSESSING SUBSURFACE TRANSPORT

a) Using Figure 5, estimate current penetration depth, d_c, given t_c, k and ν .

b) If d_w is less than d_u and d_c ($d_w < d_u, d_c$), the slug of spilled fluids has reached the water table. Go to Step 6 to assess contamination at water table.

c) If d_w is less than d_u but greater than d_c ($d_c < d_w < d_u$), the slug of spilled fluids is currently above the water table, but will reach the water table in approximately $T = t_w - t_c$ minutes. Go to Step 6 to assess contamination at water table in the event that contaminated soils cannot be removed prior to t_w. Otherwise, analysis is complete.

d) If d_u is less than d_w but greater than d_c ($d_c < d_u < d_w$), the slug of spilled fluids is currently moving downward; however, it will not reach the water table. Movement of the slug of spilled fluids will continue for approximately $T = t_u - t_c$ minutes. Analysis is complete.

e) If d_u is less than d_c and d_w ($d_u < d_c, d_w$), the slug of spilled fluids ceased movement at t_u, and did not reach the water table. Analysis is complete.

Step 6: Evaluate Contamination At/Below Water Table

a) If density of spilled fluid is greater than density of water (ρ_w = 1,000 kg/m^3), then the slug of spilled fluid will continue to migrate downward below the water table, but at a slower rate than above the water table. Any skewing of this downward migration in the direction of groundwater flow is expected to be slight. Downward movement will continue to the ultimate penetration depth, d_u, or until an impermeable layer is reached. If the latter occurs, the spilled fluid reaching the impermeable layer will spread on top of the impermeable layer in the shape of a pancake, as shown in Figure 3. Analysis is complete.

b) If density of spilled fluid is less than density of water (ρ_w = 1,000 kg/m^3), estimate size of "pancake" of spilled fluids that will ultimately occur on top of the water table.

   i) Estimate the volume of spilled fluids reaching the water table, V_w, as follows:

$$V_w = V_s \; (d_u - d_w) \; / \; d_u$$

   ii) Using Figure 7, estimate the size of the area of the "pancake" of spilled fluids floating on top of the water table, given V_w and k.

For a flat water table surface the pancake will be approximately circular, and centered about the center of the original spill area on the ground surface. For tilted water tables, the pancake will be elliptical, with the major axis of the pancake coincident with the direction of groundwater flow. Most of the spilled fluid will occur down-gradient from the center of the original spill area on the ground surface, as shown in Figure 2. Soil heterogeneities at the water table and fluctuations in the water table elevation result in greater thicknesses of spilled fluids on top of the water table, and thus, smaller pancake areas than those indicated in Figure 7. Analysis is complete.

GENERAL NOTES ON THE USE OF THE SUBSURFACE TRANSPORT NOMOGRAMS

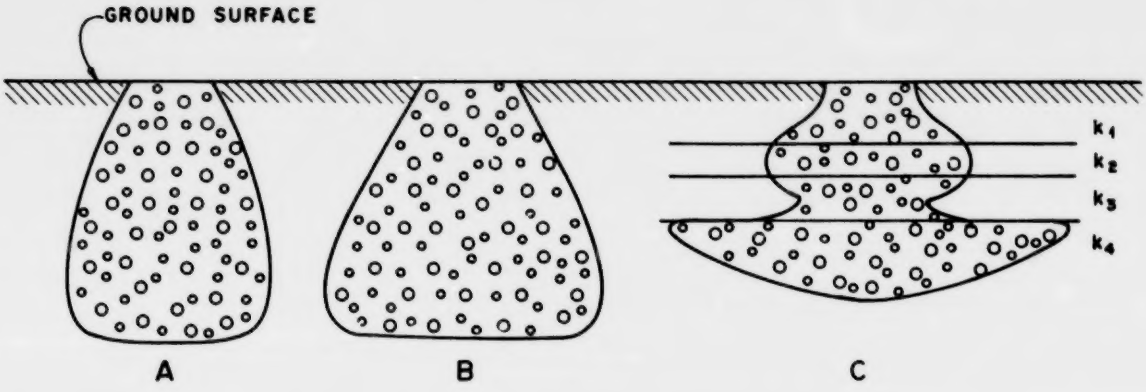
Lateral Migration - The approach to assessing the subsurface transport of oily fluids immiscible with water assumed that flow in the unsaturated zone is strictly downward, with no lateral migration. This is conservative with regard to assessing the potential for contamination at or below the water table; however, it may under-estimate the size of the area of any soils that must be excavated during clean-up operations. The potential for lateral migration in the unsaturated zone increases for: 1) decreased soil permeability, 2) increased soil heterogeneities, or 3) increased pool depth on land surface. The first two cases are illustrated in Figure 9 (API, 1972). Assuming lateral migration equal to the value for ultimate penetration depth, d_u, is usually a very conservative assumption.

Vertical Migration - Where leakage occurs from a container on a continuous basis over an extended period of time (minutes for gravels, hours to days for sands, days to months for silty sands), a situation such as that shown in Figure 10 can occur. The areal extent of the spill pool increases with time, and the depth of soil penetration at a given location is dependent on the length of time that the spill pool has existed at that location. In these instances, maximum soil penetration will generally occur directly beneath the ruptured container. The soil penetration depths and times calculated are average values for Figure 10 spill scenarios, and thus they under-estimate soil penetration for the leading edge of the front of penetrating fluids.

Impact of Fluid Density on Behaviour at Water Table - In Step 6, the fluid density for fresh water ($\rho_w = 1{,}000$ kg/m^3) was given as the threshold for spilled fluids to sink below the water table rather than float on top of the water table. In fact, fluids immiscible with water must be slightly more dense than water to sink below the water table, with the additional density (that in excess of 1,000 kg/m^3) contributing to the force required to break through the surface tension forces between the water and soil particles in the capillary fringe. Denser-than-water fluids such as Type A and D transformer Askarels (PCB-chlorobenzene mixtures) are more than 1.4 times more dense than water, and thus, these fluids are expected to sink. However, for fluids immiscible with water with densities in the range of 1.1 to 1.2 times that of water or less, it would be prudent to evaluate the ramifications of both contamination at and below the water table in Step 6.

SAMPLE CALCULATION

A 20,000 L outdoor transformer that contained PCB-contaminated mineral oil has drained through a ruptured seam. The drained transformer is discovered at 11:00 a.m. on Tuesday, and the unit was last inspected at 11:00 a.m. on Monday. No measures were installed at the site to contain leaked fluids. The


GROUND SURFACE
k_1
k_2
k_3
k_4
A
B
C

A - HIGHLY PERMEABLE, HOMOGENEOUS SOIL

B - LESS PERMEABLE, HOMOGENEOUS SOIL

C - STRATIFIED SOIL WITH VARYING PERMEABILITY

FIGURE 9 — GENERALIZED VARIATIONS IN LATERAL SUBSURFACE MIGRATION DUE TO VARIATIONS IN SOIL PERMEABILITY

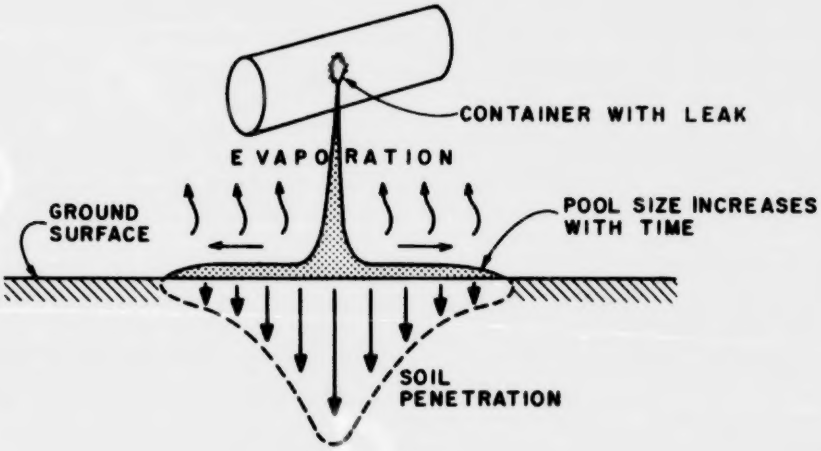

CONTAINER WITH LEAK
EVAPORATION
GROUND SURFACE
POOL SIZE INCREASES WITH TIME
SOIL PENETRATION

FIGURE 10 — POTENTIAL SPATIAL VARIATION IN SUBSURFACE PENETRATION

extent of soil and vegetation discolouration by the leaked fluids is estimated to be 100 m^2. All of the spilled fluids have infiltrated the soil surface. The air temperature is estimated to be 15°C.

Complete the worksheet shown in Figure 8 to assess the extent of subsurface contamination resulting from this spill.

Step 1: Estimate Fluid Properties

- From a figure showing mineral oil absolute viscosity versus temperature that was obtained prior to the spill, the absolute viscosity for mineral oil at 15°C is 1.88×10^{-2} Pa.sec.
- From a figure showing mineral oil fluid density versus temperature that was obtained prior to the spill, the fluid density for mineral oil at 15°C is 882 kg/m^3.
- Therefore, mineral oil kinematic viscosity = $1.88 \times 10^{-2}/882$ = 2.13×10^{-5} m^2/sec.

Step 2: Estimate Soil Data

- Based on observations of the surface soil and discussions with a hydrogeologist at a local environmental consulting firm, the soil type is estimated to be a sand, with small quantities (15 to 25 percent) of silt.
- From Figure 4, a soil permeability of 10^{-11} m^2 is selected.
- Based on discussions with the above-mentioned hydrogeologist, the water table is estimated to be 5 m below ground surface.

Step 3: Estimate Spill Data

- The elapsed time since the occurrence of the spill is conservatively estimated as being 1 day, because this is the length of time since the unit was last inspected.
- The volume of fluids spilled is 20,000 L, or 20 m^3
- The area of the spill pool was 100 m^2
- Therefore, the volumetric loading was 20/100 = 0.2 m

Step 4: Estimate Potential Subsurface Penetration Depths and Times

- Using Figure 6, the ultimate penetration depth is estimated to be 10 m (assuming no water table is encountered).
- Using Figure 5, 1.0×10^4 minutes (7 days) are required for the ultimate penetration depth to be attained (assuming no water table is encountered).
- Using Figure 5, 5.0×10^3 minutes (3.5 days) are required for the PCB-contaminated mineral oils to reach the water table.

Step 5: Evaluate the Current Status of Subsurface Penetration

- Using Figure 5, the depth to which the PCB-contaminated mineral oils have penetrated (ie. after 1 day) is 1.4 m.
- Scenario 2 ($d_c < d_w < d_u$) represents the current status of subsurface penetration, in that the penetrating mineral oils are currently above the water table; however, they will reach the water table in T = 3.5 - 1 = 2.5 days

Step 6: Evaluate Contamination At/Below Water Table

- Mineral oil is less dense than water, thus Scenario 6 applies.
- The volume of PCB-contaminated mineral oil that will reach the water table is [(10-5)/10]20 = 10 m^3.
- Using Figure 7, a 620-m^2 "pancake" of PCB-contaminated mineral oils would ultimately result on top of the water table if no spill clean-up measures are implemented.

CONCLUDING REMARKS

The STRAM for spills of oily fluids that are immiscible with water is a first-cut predictor, and the model results should be used accordingly. Spill clean-up measures should be implemented at a spill site as soon as possible, regardless of the potential extent of soil and groundwater contamination.

User preparation and training is important to develop a familiarity with the model assumptions, types of input data required, the nomograms and the step-by-step procedures for assessing subsurface contamination in advance of any spill situations. To the extent possible, model input data (eg. fluid properties) and lists of contact persons (eg. local hydrogeologists/geotechnical engineers) should be obtained at this time.

When applying the model, ranges of values should be used for the model parameters in instances where the values of those parameters are uncertain. The resultant ranges in predicted penetration depths and times represent the uncertainty in subsurface contamination, given the uncertainties in the input parameter values.

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ADAPTION AND APPLICATION OF A DENSE GAS DISPERSION MODEL - DEGADIS

by

N.M. To and M.A. Fitch
Research Department
Esso Resources Canada Limited
Calgary, Alberta

and

C. Micek
Esso Chemical Alberta Limited
Redwater, Alberta

ABSTRACT

A heavier than air gas (HTAG) dispersion model Degadis has been selected to be developed into an emergency response tool. The adaptation of the model to run on an IBM P.C. - AT was successful. Benchmark applications of the model, however, showed that its speed in some cases needs to be improved. Other possible improvements are recommended.

INTRODUCTION

Since the Bhopal incident in 1984, there has been a corporation-wide effort to strengthen our emergency response capability in accidental toxic chemical spills. Esso Resources Canada Limited, Esso Chemical Alberta Limited and other North American affiliates have been promoting and participating in the development of an improved heavier than air gas (HTAG) dispersion model. This paper outlines some of the work involved in the selection and adaptation of a HTAG model, Degadis, (1) for use on a personal computer. The goal is to have a validated HTAG model, such as Degadis, used for real time emergency response in the near future.

Model Selection

Existing P.C. version of both proprietary and non-proprietary HTAG models were surveyed. (During the survey, whether or not proprietary models were validated was difficult to assess.) The emphasis of the selection was then shifted to non-proprietary models. The only model of this nature for HTAG available at the time was the Ontario Ministry of the Environment (OME) puff model (2). The OME program runs on either the Osborne I or IBM P.C., and is a top hat model for instantaneous release of HTAG. A top hat (or box) model treats the cloud of heavier than air gas released in an accidental spill as a vertical cylinder or a plume with a predetermined geometric cross section (e.g. rectangular) and a uniform concentration within the plume. The height and width of the plume change with gravity spreading and air entrainment.

The advantage of the OME model was computational speed (under 3 minutes for some simulations). However, model results were thought to be unconservative (3), and more validation against dispersion data was required. The model was unable to simulate continuous release of HTAG.

Havens and Spicer developed the HTAG model Degadis (an acronym for dense gas dispersion) in 1985 (1). Degadis is an advanced similarity model, which simulates the HTAG cloud by assuming that a source cloud forms over a liquid pool, spreads by negative buoyancy and mixes with air to form a uniformly mixed source blanket. Wind picks up gas from the source blanket and generates a vapour cloud with Gaussian concentration profiles. Degadis has been validated against extensive field and laboratory data (1), and it can simulate continuous or spontaneous releases of HTAG. The programs were developed under VAX/VMS V3.5 and VAX-11 Fortran V3.5. Since to the authors' knowledge there was no existing personal computer version of Degadis, the work to modify Degadis to run on an IBM personal computer was initiated.

Prior to the author's adaptation of Degadis, Exxon Research and Engineering Company (ER & E) at New Jersey was in the process of modifying Degadis to work in an IBM TSO environment. This TSO developmental version of Degadis was used to construct the P.C. model.

Hardware/System used for P.C. Degadis

The program was developed on the Zenith personal computer (IBM P.C. AT compatible) using RM Professional Fortran (4). The personal computer was equipped with a numeric co-processor (80287) with one floppy disk drive and one 20 Megabyte hard disk drive. Any compatible computer system may be used to run the program. A disk operating system (DOS) of 2.10 or higher may be used with RM Fortran.

Organization of the Programs

The organization of P.C. Degadis is different from that of the Havens and Spicer version (1, Vol. III). Some details of the differences may be found in

Appendix A.

In addition, the P.C. program has been modifed to conform to the American National Standard Programming Language Fortran /77. IBM extensions used in the ER & E developmental program were changed to accommodate RM Fortran restrictions. (4)

Limitation and Performance of P.C. Degadis

P.C. Degadis (Dega) is essentially the same as VAX Degadis, hence the original work on validation still applies. However, because of the limitation in IBM P.C. AT RAM memory (640 k), the sizes of the matrices must be limited. Two of the variables that determine the matrix sizes are MAXNT (Maximum No. of distances per observer) and MAXNOB (maximum No. of observers) in Degpar. Values of these two variables control the size of required memory (e.g. when MAXNOB = 9 MAXNT = 180 the required memory is 483 k). For microcomputers which have extended memory boards or for super micros which have virtual memory, the problem of memory sizes is not crucial.

Table 1 below shows the speed comparison between P.C. and mainframe Degadis for benchmark applications to sample transient and steady state cases. Even though in the transient case the time ratio usually improved over the steady state case, the elapsed time of 52 min. 57 sec. is too long for P.C. Degadis to be useful as a real time response tool.

TABLE 1

Speed Comparison Between Mainframe (TSO) and P.C. Degadis

	Sample Transient Case (Elapsed Run Time in Sec.)	Sample Steady State Case (Elapsed Run Time in Sec
Mainframe TSO Version*	252.3	6.3
P.C. AT Version	3177.0	290
Time Ratio Mainframe to P.C.	1:12.6	1:46.0

* N.B. Mainframe version has slightly more output than P.C. version

When executing Degadis, a significant amount of computation time is spent in iterative loops around a numerical integration code. The existing integration scheme in Degadis is a fourth order Runge-Kutta algorithm. A good time-saving measure would be to substitute a faster integration scheme into the P.C. programme.

Before Degadis can be run, the source strength of a spilled chemical and/or a generated vapour cloud must be known. A separate front-end model is needed to obtain this information. However, estimating the factors that control the flow rate of spilled chemicals, such as the size and location of the rupture in a tank car, whether single (gas only) or two-phase (gas and liquid) flow is occurring, and whether the pressure driving the flow through the hole is constant or decreasing with time, is a very difficult task in an emergency situation. There is no easy solution to this problem. Extensive training of operators to assess source strengths in an emergency using visual and computational methods seems to be a solution. It is also possible that remote sensing instruments with suitable software may assist in calculating the size, volume and rate of growth of toxic gas clouds.

However, it is conceivable that operators may make mistakes in assessing input parameters to Degadis. The program may abort with error messages in these cases. The existing error messages are often not detailed enough and one may have to refer to Appendix D of Vol. III of the reference manuals (1) for more diagnostic messages. This may be too time consuming for emergencies. For the P.C. version, materials in Appendix D Vol. III should be appended to the error messages so that the source of the problem affecting P.C. Degadis may be determined quickly.

RECOMMENDATIONS

In order to make P.C. Degadis an effective real time HTAG dispersion prediction tool, the following are recommended:

- improve the diagnostic message when program aborts
- add a versatile and conservative source model
- streamline integration scheme and related code for speed;

- add graphics to display results

With these changes, P.C. Degadis will become an effective tool in emergency response for heavier than air gas.

ACKNOWLEDGMENT

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APPENDIX A

Organization of P.C. Degadis

The original VAX/VMS Degadis is comprised of 5 separate programs: Degadis, Degadis1, Degadis2, Degadis3 and Sdegadis2. A series of input files containing convergence criteria, initial increments, etc. supply Degadis with the necessary numerical parameters for a simulation. Details of these programs may be found in (1, Vol. III).

The organization of P.C. Degadis is somewhat different. It consists of two main programs: Dsetup and Dega.

Dsetup is run interactively. The user specifies information about the environment (wind speed, temperature, atmospheric pressure, etc.); the modelling details (observor sorting details for transient release, initial gas mass, etc.); gas composition and properties and other details of the physical description of the gas release. Dsetup formulates the user-supplied information into an input file for program Dega.

Program Dega is, in fact, a combination of the previous VAX programs DEGADIS 1, 2, and 3 and SDegadis2. Within Dega, the main program is DEGA1 which calls up subroutines and functions to perform transient or steady state dispersion simulations. Most of the common blocks for Dega have been collected in a separate program named DEGCOM. Some parameters for the transient case have been gathered in the programme called DEGPAR. DEGCOM and DEGPAR are inserted into the main program and subroutines during compilation by means of include statements. The series of input files in the original programs containing numerical parameters have been incorporated into Dega. A data block in the main program of Dega supplies the parameters as well as additional constants required by the program. Sample values of VALUE1 parameters are shown on the following list:

```
DATA OUTSZ/.4/
DATA VONKAR/.35/,G/9.81
DATA SYOER/.03/,ERRO/.005/,SZOER/.01/,WTAIO/1.0/,WTQOO/1./,
WTSZO/1./,ERRP/.003/,SMXP/10./,WTSZP/1./,WTSYP/1./,WTBEP/1./,
WTDH/1./,ERRG/.003/,SMXG/10./,ERTDNF/.0005/,ERTUPF/.0005/,
WTRUH/1./,WTDHG/1./
 DATA STPO/.05/,STPP/.05/,ODLP/.06/,ODLLP/80./,STPG/.05/,
ODLG/.045/,ODLLG/80./
DATA STPIN/.01/,ERBND/.0025/,STPMX/5.12/,WTRG/1./,
WTTM/1./,WTYA/1./,WTYC/1./,WTEB/1./,WTMB/1./,WTUH/1./,
XLI/.05/,XRI/.4/,EPS/.001/,ZLOW/.01/,STPINZ/-.02/,
ERBNDZ/.005/,STPMXZ/-.04/,SRCOER/.070/,SRCSS/5.2/,SRCCUT/.0001/,
HTCUT/.1/,ERNOBL/1.0005/,NOBLPT/100./,CRFGER/.008/,
EPSLON/.59/
DATA CE/1.15D/,DROMIN/.025/
DATA SZSTPO/.01/,SZERR/.001/,SZMX/5.0/,SZSZO/.01/
DATA ALPCO/.2/,IALPFL/1./
DATA DELLAY/2.15/,IPHIFL/3./
DATA VUA/1.3/,VUB/1.2/,VUC/20./,VUD/.64/,VUDELT/.2/
```

Explanation of the variables may be found in (1, Vol. III)

MODELLING THE EVAPORATION OF VOLATILE LIQUIDS AND SPREADING OF CHEMICALS ON SNOW AND ICE

P.I. Kawamura, D. Mackay

Dept. of Chemical Engineering and Applied Chemistry
University of Toronto
Toronto, Ontario

ABSTRACT

This paper describes studies of two aspects of the short-term behaviour and fate of chemicals resulting from terrestrial chemical spills.

In the first study, two novel models have been developed to estimate the evaporation rate of volatile and non-volatile liquids. Both models are based on steady heat balances around the chemical pool and include the effects of solar insolation, evaporative cooling, and heat transfer from the ground. The simpler of the two, the "direct evaporation" method, estimates the evaporation rate directly from available physical-chemical data. The second model, the "surface temperature" method, determines the surface temperature of the evaporating pool by an iterative procedure. This temperature is then used to estimate the evaporation rate.

Experiments are described in which the evaporation rates of seven volatile chemicals were measured from pans under known meteorological conditions. The two models and the experimental evaporation rates were in satisfactory agreement, with an average difference of 19% for the direct evaporation method, and 13% for the surface temperature method. It is concluded that either model can be used to estimate evaporation rates under actual spill conditions.

In the second study, a relatively simple model has been developed to describe the spreading of liquid chemicals on snow and ice. Experiments were performed on snow and ice surfaces to determine the spreading behaviour and characteristics and the general phenomena which occur when various chemicals are spilled on these surfaces.

The final spill area and the spreading rate results were correlated with the spill volume, chemical viscosity and snow depth and properties, in dimensional and dimensionless form. These correlations can be viewed as comprising part of the general spreading model, and are believed to enable predictions to be made of the spreading behaviour for most chemicals under actual spill conditions.

1. INTRODUCTION

Accidental spills of hazardous and toxic chemicals present a serious risk to the public's safety and to the environment. An immediate concern is the generation of an excessive chemical vapour concentration downwind of the spill, which may cause health and fire hazards. To estimate this exposure concentration, the evaporation rate, or the source strength, which is the product of the evaporation flux of the chemical and the spill area must be determined. This paper treats two aspects of this issue: development of a method for predicting the evaporation rate per unit area of pure volatile chemicals resulting from ground spills, and an exploratory investigation of the spreading behaviour of chemicals when spilled onto snow and ice surfaces.

When quantifying the evaporation of volatile liquid, an important factor to consider is the evaporative cooling of the chemical. For volatile chemicals, there is often a considerable decrease in the temperature of the pool as the system self cools to obtain the heat of evaporation.

For example, an experiment performed in this study under environmental conditions in which pentane was allowed to evaporate from a flat pan showed that the pool temperature can drop as much as 30°C below the ambient temperature. This will introduce an error of approximately a factor of four in the calculation of the evaporation rate if this cooling effect is neglected.

The first part of the study was performed to develop and verify a simple formula or procedure which can predict with acceptable accuracy the evaporation rate of pure liquid chemicals resulting from ground spills under various environmental conditions. It should be noted that no other model exists which incorporates the evaporative cooling effect, as well as other factors such as solar insolation and ground conduction from available data.

The second part of this study concerns the spreading behaviour of chemicals when spilled onto snow and ice, a common ground surface in much of Canada for much of the year. When planning for, or responding to, chemical spills, it is useful to know the likely spreading characteristics of the chemical. In particular, it is helpful if the final spill area and the time necessary to reach that area can be predicted. Any special or unusual spill characteristics of the chemical such as tendency to react, or evaporate rapidly should also be known in advance.

Estimating the final spill area for spills on snow and ice is particularly important since the spill area is difficult to detect by eye for most liquid chemicals. On a snow surface, the chemical may penetrate downward in the snow and spread invisibly along the bottom of the snowcover.

There are additional effects that must be considered in the event of a chemical spill on snow and ice covered surfaces, as opposed to a spill on a ground surface. The most important is the extent to which the chemical interacts with, or dissolves snow/ice. For example, chemicals which are completely miscible with water, such as low molecular weight alcohols, will readily dissolve snow and ice, which results in an increase in spill volume. These chemicals, if spilled on or near a snow or ice covered body of water, may "eat through" the snow and ice to the underlying water. Furthermore, a strong acid may release sufficient heat to melt an appreciable quantity of ice.

Kawamura and Mackay's spreading report (report EE 79 published by Environment Canada, 1986) proposed a classification system to categorize chemicals based on their ability to dissolve snow and ice. By combining the literature water/ice in chemical solubility data and data obtained by performing simple solubility measurements, most of the chemicals on Environment Canada's Priority Hazardous Materials were classified into one of three groups:

Group 1: chemicals less than 5% solubility by mass
Group 2: greater than 5% but not completely soluble
Group 3: completely soluble.

This part of the study is concerned with the understanding and the prediction of the behaviour of chemicals when spilled on snow and ice. This paper addresses the following objectives:

i. to describe the general phenomena which occur when various chemicals are spilled on ice and snow,
ii. to provide methods to estimate the final spill area as a function of spill volume and other properties (This study is concerned with instantaneous spills, or spills in which a finite volume of chemical is released rapidly, as opposed to a continuous leak spill.),

iii. to estimate the time of spreading, and
iv. to develop a model of general spill behaviour.

2. MODEL DEVELOPMENT

In this paper, only a brief description of the evaporation and spreading models is given. Complete details are documented in Kawamura and Mackay (1986).

2.1 Evaporation Rates

Two relatively simple evaporation models were assembled to predict the evaporation rate from ground spills. These are termed the "direct evaporation" method and the "surface temperature" method. Both models are based on a quasi steady state heat balance around the chemical pool, which includes the effects of solar insolation, sensible heat transfer from the ground and air and evaporative cooling. Existing equations and correlations were gathered from the literature for each of these heat transfer terms.

i. Direct Evaporation Model. The direct evaporation model estimates the evaporation rate directly from the following equation:

$$E = E_r\ [1/(1+\beta)] + E_a\ [\beta/(1+\beta)] \qquad (2.1)$$

where E is the evaporation rate. The terms E_r and E_a can be viewed as the rate at which the chemical can be evaporated as a result of solar insolation and by assuming that the pool surface temperature equals the air temperature, respectively.

The key variable is β which controls the relative contributions of E_r and E_a. If β is small compared to unity E approaches E_r, while if β is larger E approaches E_a. Although the term β is the result of simplifying assumptions and algebraic manipulations, it can be shown to be approximately inversely proportional to the vapour pressure.

Thus, a substance of high vapour pressure (eg. pentane) will have a small β and E tends to be dominated by E_r. Such substances tend to have large evaporative cooling effects. Low vapour pressure, high boiling point liquids will have a larger β and E is dominated by E_a, the air-pool temperature difference being small.

The advantage of this model is that it is simple and requires no iteration.

ii. Surface Temperature Model. This model determines the surface temperature of the pool numerically, based on the following steady state energy balance:

$$Q_{sol} + Q_{atm} - Q_{sur} - Q_e + Q_{sen} + Q_g = 0 \qquad (2.2)$$

where Q_{sol} is the net solar radiation (corrected for the amount reflected from the surface), Q_{atm} is the long-wave radiation from the atmosphere absorbed by the pool, Q_{sur} is the long-wave radiation emitted by the pool, Q_e is the evaporation energy, Q_{sen} is the sensible heat conducted into the pool from the atmosphere, and Q_g is the heat conducted from the ground. Of these energy terms, all but Q_{sol} and Q_{atm} are functions of the surface temperature. This temperature is then used to calculate the evaporation rate. The computation involves employing a standard root determining procedure, such as the Newton's method, which was used in this study.

This procedure is best suited for a computer but the program required is very short and simple. Despite having to use a computer or a programmable calculator in this method, it has advantage of including all the energy exchange terms that are present in the overall energy balance.

2.2. Spreading Models

The spreading behaviour of a chemical on snow, ice or absorbing terrain is a very complex phenomena. Thus, it is likely that several models will be devised, each with a desired level of accuracy. In this study, a novel general model is introduced which includes absorption, evaporation and snow and ice dissolution.

In this model, a basic area-time relationship is proposed of the form:

$$A = A_f \ (1-\exp(-(\tau/\gamma)^x)) \qquad (2.2)$$

where A is the area, A_f is the final area, τ is the time, and γ and x are constants. Regardless of the value of x, the area is 63% of the final area when τ equals γ. γ is thus a "spreading time constant". Increasing x slows down the initial spreading and accelerates the later spreading. It controls the slope of a A-τ graph when γ equals τ, a large value of x giving a large slope.

The final area, A_f, is estimated from the initial spill volume (V), the volume change (until spreading stops) due to evaporation, absorption, snow dissolution, and a final equilibrium spill depth on the surface (h_f), such that

$$V - \Delta V = A_f \ h_f \qquad (2.3)$$

ΔV is estimated as the algebraic sum of loss due to evaporation (h_e A_f), loss due to absorption in soil (h_a A_f) and gain due to dissolution of snow (h_s A_f). Expressions are postulated for these terms in the spreading report (Kawamura and Mackay, 1986).

The spreading time can be approximated by determining the time when the area equals 95% of the final area, using equation 2.2. The spreading time, τ_f is:

$$\tau_f = \gamma \ . \ 3^{1/x} \qquad (2.4)$$

In this study, the final spill area and the spreading rate for chemicals on ice and snow were investigated. In particular, the experimental data were gathered to correlate the final spill thickness, h_f, (or A_f, with h_e, h_a, h_s equal to zero), and the spreading time constant, with parameters such as the spill volume, chemical viscosity and snow properties. The experimental slope value, x, was also determined.

It should be noted that no other spreading model contains terms for all these processes.

3. EXPERIMENTAL

3.1 Evaporation Experiments

Two sets of evaporation experiments were performed at the Environment Canada Atmospheric Environment Services experimental site in Woodbridge, Ontario. The procedure involved allowing selected chemicals to evaporate from a flat circular pan under various environmental conditions.

In the first set of experiments, the effect of ground conduction on the evaporation rate was eliminated by placing a styrofoam board under the evaporation pans. The metal pans, with the inner surface painted black, were of diameters 0.61 and 0.91 m and depth 5 cm. The choice of the pan size used in specific experiments was based on the relative volatility of the chemical and the prevailing atmospheric conditions. The following chemicals were used: toluene, cyclohexane, hexane, methanol, n-pentane, dichloromethane, and Freon 11 (trichlorofluoromethane). The evaporation rate was measured by a device which consisted of a 6 L glass reservoir, initially filled with the cheical at ambient temperature, and a glass tube, which served to connect the reservoir and the evaporating chemical in the pan. This device maintained a constant level of chemical in the evaporation pan by replacing the evaporated chemical by additions of chemical from the reservoir. The evaporation rate was determined by observing the volume changes in the reservoir over the duration of the experiment.

In the second set of experiments, a pan, 0.46 m in diameter with a height of 10.2 cm was used. The pan was filled to a depth of 5 cm with sand, and was then partially buried in the ground so that the surface of the sand was just slightly higher than ground level. Before the experiment, the sand was saturated with water to avoid sorption of the chemical into the sand matrix. Either four or seven litres of the chemical, with the same initial temperature as that of the surroundings, were then introduced onto the sand surface. The chemicals used in these experiments were: n-pentane, toluene, hexane, cyclohexane, and Freon 11. The evaporation rate was determined by measuring the volume of chemical remaining in the pan, at the termination of the experiment.

In addition to the evaporation rate, the bulk pool and surface temperatures were measured for both sets of experiments, as well as the sand temperatures at three different depths in the ground conduction experiments. Atmospheric data, such as air temperature, solar insolation (for the first set of experiments), cloud cover, average wind speed, and relative humidity were also recorded, the latter from the weather office. In the first set of experiments, all data, including the evaporation rate, were averaged over a time interval of 30 to 60 minutes for each experiment after "steady state" conditions were reached. In the second set of experiments, the data were averaged over the entire duration of the experiment.

The recorded data, with the exception of the solar insolation, surface, pool and ground (sand) temperatures, were used as input data for the two evaporation models. The model predictions were then compared to the experimental evaporation rate. Data not used in the model predictions were used to calculate and compare the existing equations and correlations used in the model to the experimentally determined values.

3.2 Spreading Experiments

3.2.1. Spreading on Ice. Initial ice spreading experiments involved spilling various chemicals on a small scale on artifically prepared smooth and rough ice surfaces. This was followed by several large outdoor spills on ice.

(i) Spreading on Artifically Prepared Ice Surfaces. Small-scale spreading experiments were performed on artifically prepared smooth and rough ice surfaces.

Two different surface roughnesses were employed: 0.5-1 mm and 1-2 mm. The ice surfaces (dimensions 61 x 61 cm) were prepared as described in Kawamura and Mackay's spreading report.

The chemicals selected for this study were m-xylene, n-pentanol, heavy USP mineral oil (viscosity: 1500 cp at -5°C), and a white mineral oil called Bayol 35 (8 cp at -5°C). These chemicals were chosen on the basis of low solubility of ice, small evaporation rate, a relatively non-hazardous nature and their wide range of viscosities (0.9-1500 cp). The volume of chemical used was 25 and 50 mL for spills on smooth ice and 50 mL for each chemical on each of the two rough ice surfaces. A new ice surface was prepared and used for each spill.

The chemicals were spilled from a 2.2 cm ID by 20 cm glass tube at room temperature. A rubber ring was attached to one end of the glass tube and the rubber end of the tube was placed firmly against the glass surface. A pre-determined volume of liquid was then poured into the tube. Time was recorded with a stopwatch, which was started, when the tube containing the liquid was lifted.

A video camera was used to record the spreading and stopwatch readings. At the termination of spreading, the final spill dimensions were recorded.

(ii) Outdoor Ice Spreading Experiments. Large-scale outdoor spreading experiments on ice were conducted on a 2.4 x 2.4 m plastic-sealed wooden platform. Water was poured onto this platform to produce an ice surface approximately 1.5 cm thick.

The ice surface was "marked off" at 10 cm intervals in eight directions from the centre. In total, six experiments were performed, using five different chemicals. The chemicals and the volume spilled were: m-xylene, 450 mL and 1 L; n-pentanol, 1L; Bayol, 700 mL; light mineral oil (viscosity 450 cp at -5°C), 2L; and ethylene glycol, 750 mL.

The discharge of the chemical onto the ice surface involved pouring the chemical into a large funnel, with a 5 cm flexible plastic tube attached to the end. The discharge end of the tube was positioned to a few centimetres above the centre of the ice surface and the discharge time for most of the chemicals spilled was less than five seconds.

During the initial period of spreading, the dimensionas of the spill were recorded with a video camera, but after several minutes, the spill distances were recorded by hand. The initial chemical and air temperature, as well as the general meteorological conditions were also noted and recorded. After each experiment, the ice surface was wiped clean and additional water was added to form a new layer of ice. The ice surface was relatively smooth for most experiments, although several "rough" (<1 mm) areas were observed for some experiments.

3.2.2. Spreading Experiments on Snow. The snow spreading experiments involved the use of two impermeable surfaces, glass and ice, to act as a base for the snowcover. The spreading rate and characteristics were observed and quantified with respect to these surfaces.

(i) Snow-on-Glass Spreading Experiments. It is believed that there are many variables which affect the spreading of chemicals in snow media. In this study, experiments were performed to determine the effect of the following variables (experimental range of these variables indicated in brackets) on the final spill area and spreading rate: spill volume (0.5-3 L), chemical viscosity (0.9-1500 cp), snow density (0.12-0.42 g/mL), snow depth (4-30 cm), and the type of snow (from fresh, "crystalline" snow flakes to rounded 2-4 mm diameter snow crystals). Due to time limitations, experiments to determine the effect of spill release rate were not performed. However, the five variables studied are believed to be the major parameters which determine the spreading characteristics.

Bayol (white mineral oil) was the chemical used in all of these experiments with the exception of the chemical viscosity experiments, which involved four other insoluble chemicals: xylene, n-pentanol and light and heavy mineral oil. In each of the five sets of experiments, an attempt was made to keep all other experimental conditions constant.

The apparatus consisted of a 91 x 91 cm smooth glass sheet in which a grid consisting of 1 cm markings originating from the centre was drawn in eight directions. This glass sheet was placed on a wooden frame and the glass on this frame was supported by two, one metre high tables. The snow was placed on top of the glass, and the spreading of chemicals (which were dyed red) was observed from a mirror positioned at an angle under the glass.

Unlike the ice experiments, the spreading rate was slow enough such that all spill dimensions were recorded by hand at regular time intervals. In addition, the penetration time, which was defined as the time for the chemical to penetrate to the bottom of the snowcover, and the extent of spreading on the surface of the snow were recorded. Snow and air temperatures were also monitored throughout the experiment. After each experiment, a cross section profile of the chemical in the snow was made and observations recorded.

These experiments were followed by several experiments using three water-soluble chemicals: sulphuric acid (100 mL), ethylene glycol (200 mL) and ethanol (200 mL). The same experimental procedure was followed for these experiments.

3.2.3. Snow-on-Ice Spreading Experiments.

Two spreading experiments on snow covered ice surfaces were conducted on the same ice surface that was used in the large-scale ice experiments, as described previously. Instead of a grid to mark the dimensions of the spill, wooden sticks were stuck into the snow at 10 cm intervals. The chemicals were discharged onto the snow in the same manner as in the large-scale ice experiments.

The first experiment involved spilling 3 L of bayol (a while mineral oil) onto 9 cm of snow. The extent of spreading on the underlying ice surface was determined by checking for red-dyed Bayol-snow mixture by using the wooden sticks as a "dipstick". After cessation of spreading, the final spill are was accurately determined by removing the snow.

The second experiment involved spilling 1 L of 85% ethanol onto 11 cm of snow. The wooden sticks were again used to determine the extent of spreading but they were tested for the smell of ethanol instead of the red dye. In addition to the spreading rate, the temperatures and general observations of the ethanol-water-snow mixtures were recorded. The spreading was allowed to proceed to completion and the state of the snow and ice surface, as well as the final spill area was observed and noted.

4. RESULTS AND DISCUSSION

4.1. Evaporation Experiments

4.1.1. Evaporation Experiments Without Ground Conduction.

The experimental data were averaged over a time period of one half to one hour for each experiment after "steady state" conditions were reached. The specific time interval depended on the duration of the experiment, which lasted from one to three hours. During this time, up to 6 L of the chemical were evaporated.

These experimental results (given in Table 1 in increasing order of chemical volatility) were compared to the evaporation rates predicted by the direct evaporation and surface temperature models. It was found that in most experiments, "steady state" was reached in less than 15 minutes after commencement of the experiment.

The results suggest that both the direct evaporation method and the surface temperature method predict evaporation rates which generally agreed well with the experimental evaporation rates under both summer and winter conditions. The difference between the predicted and the experimental rates varied from 0 to 40%, with an average of 17% for the direct evaporation method and 1 to 32%, with a 12% average for the surface temperature method. This error is judged to be acceptable for models applied under environmental emergency conditions.

TABLE 1

SUMMARY OF EVAPORATION RATE (kg/m^{2}h) RESULTS AND MODEL PREDICTIONS FOR EXPERIMENTS WITHOUT GROUND CONDUCTION

		AIR	MODEL PREDICTIONS				
EXP.	CHEMICAL	TEMP °C	D. EVAP.	(% DIF)	S.TEMP	(% DIF)	EXPERIMENTAL
1	Toluene	21	4.97	(11)	4.63	(3)	4.49
2	Toluene	29	4.63	(37)	4.46	(32)	3.39
3	Cyclohexane	24	6.41	(9)	6.21	(5)	5.89
4	Cyclohexane	25	6.23	(6)	6.13	(4)	5.89
5	Hexane	-5	5.68	(2)	5.65	(2)	5.55
6	Hexane	22	10.90	(0)	13.00	(19)	10.88
7	Methanol	7	2.35	(1)	2.67	(4)	2.55
8	Dichloromethane	-6	7.26	(23)	9.57	(1)	9.49
9	Dichloromethane	1	6.69	(11)	6.07	(19)	7.53
10	Dichloromethane	21	13.91	(15)	19.20	(18)	16.27
11	Dichloromethane	25	15.60	(13)	19.90	(11)	17.98
12	Pentane	1	7.22	(31)	8.39	(20)	10.52
13	Pentane	5	4.19	(39)	5.67	(17)	6.84
14	Pentane	7	4.97	(39)	6.64	(18)	8.13
15	Pentane	9	6.18	(40)	8.30	(20)	10.41
16	Freon 11	0	29.67	(10)	38.22	(16)	33.01
17	Freon 11	17	38.79	(18)	35.79	(2)	34.93

As expected, the surface temperature model was more accurate then the simpler direct evaporation model. Table 1 reveals that the two predictions for moderately volatile chemicals (experiment no. 1-7) were excellent, with the exception of experiment no. 2. However, the model predictions for experiments involving very volatile chemicals (experiment no. 8-17) were, in general, not as successful. This is particularly apparent in the direct evaporation model, which underpredicted the evaporation rates for all of these experiments. This underestimation of the evaporation rates can be attributed mainly to the assumption made in the direct evaporation model that the slope of the vapour pressure curve for the chemical is linear. The error introduced from this approximation is most significant for very volatile chemicals due to the large temperature difference between the surface and the air temperature.

4.1.2. Ground Conduction Evaporation Experiments. The average experimental evaporation rate, which included the effects from conduction from the ground, was compared to the predicted evaporation rates determined from the two evaporation models. The results are presented in Table 2, along with the air temperature, the duration of the experiment, and the initial volume of the chemicals used.

The results in Table 2 are similar to the results obtained in the first set of experiments (Table 1). Both models were able to predict the evaporation rate fairly accurately with the surface temperature method being the more accurate. The direct evaporation model was, again, found to underpredict the evaporation rate for the very volatile chemicals; pentane, and Freon 11. It should be noted that the experimental evaporation rate in this set of experiments is the average evaporation rate for the experimental duration, unlike the steady state evaporation rate in the first set of experiments.

The magnitude of the ground conduction and other energy terms is given in Table 3. These terms, with the exception of solar insolation, were determined from the surface temperature predicted by the surface temperature model.

It is clear that the thermal conduction from the ground accounts for a significant portion of the incoming energy for very volatile chemicals (experiments 21 to 23) and is comparable in magnitude to the sensible heat gain from the air for less volatile chemicals. As expected, the effect of ground conduction, as well as heat transfer from the air and the evaporation energy is greater for chemicals of high volatility.

The experiment involving toluene (experiment no. 18) illustrates the opposite of evaporative cooling, which may be termed, "solar heating" of the pool. This usually occurs when low volatility chemicals are exposed to high solar insolation, which results in higher pool temperatures, relative to the air temperature. Comparison of the experimental toluene pool temperatures with the air temperatures confirmed this effect. Instead of energy being conducted to the pool from the air and ground, as in experiments 19 to 23, energy was lost from the toluene pool by these two routes. Both models included this effect for this experiment by predicting an evaporation rate that corresponded to a surface temperature which was greater than the air temperature.

Finally, in the direct evaporation model, it was assumed that the net long-wave energy contribution, (Qatm-Qsur) is relatively small and considered negligible. The results obtained from these set of experiments, although not conclusive, seem to justify this assumption. This radiative energy term, however, is still employed by the surface temperature model since the required computation does not significantly increase the complexity or the computation time.

TABLE 2

RESULTS AND MODEL PREDICTIONS (kg/m^2h) FOR GROUND CONDUCTION EXPERIMENTS

EXP.	CHEMICAL	AIR TEMP °C	INITIAL VOLUME (L)	TIME (HR)	MODEL PREDICTIONS				AVERAGE EVAP. RATE
					D.EVAP	(%)	S. TEMP	(%)	
18	Toluene	25	4	3.5	5.42	(39)	4.95	(27)	3.90
19	Cyclohexane	29	4	1.67	9.92	(6)	10.44	(11)	9.38
20	Hexane	27	4	1.5	8.93	(23)	9.30	(28)	7.28
21	Pentane	23	7	1.07	15.94	(31)	22.08	(4)	23.00
22	Pentane	25	4	0.58	20.69	(24)	27.52	(2)	27.10
23	Freon 11	31	7	1.5	30.15	(14)	36.42	(4)	34.88

TABLE 3

ENERGY TERMS (kJ/m^2h) FOR GROUND CONDUCTION EXPERIMENTS

EXP. NO.	CHEMICAL	Qsol	(Qatm-Qsur)	Qsen	Qg	Qe
18	Toluene	3140	-410	-390	-180	2160
19	Cyclohexane	3220	17	620	330	4190
20	Hexane	2620	20	370	420	3430
21	Pentane	2330	320	3200	2530	8380
22	Pentane	3100	290	3300	3810	10490
23	Freon 11	3070	220	930	2580	6800

4.1.3. Model Application. Since both the direct and surface temperature models were able to estimate the evaporation rate within the accuracy required for chemical spills, either model could be employed in actual spill situations. The models may be used with confidence for liquids with boiling points which exceed 10°C below ambient temperatures. Caution should be applied when using these models below this temperature. Since the effects of boiling, freezing of the ground, and the formation of dense vapour clouds are not included, these models should not be used for chemicals such as natural gas, chlorine and propane.

The main advantage of both models is that the amount of input data required is small, and readily obtainable. In terms of convenience, the direct evaporation method is the preferred model because it does not require a computer. It is therefore useful in the rapid prediction of the evaporation rate, and at locations where a computer cannot be used, such as at the spill site. On the other hand, since more accurate results were obtained using the surface temperature model, this method may prove to be valuable for those seeking a more thorough and accurate estimate. Therefore, both models are useful, and the model to use will likely depend on personal preference, accuracy desired, convenience, and application.

4.2. Spreading on Ice Surfaces

The results of the spreading experiments on artificially prepared smooth and rough ice surfaces and large scale outdoor experiments were combined to describe the spreading characteristics with properties of the chemical and the spill volume. Specifically, the final area, A_f, the spreading time constant, γ, and the slope term, x, were correlated using the data obtained.

4.2.1. Correlation of the Final Spill Area on Ice. Based on the results of the preliminary spreading experiments performed on glass, as described in Kawamura and Mackay's spreading report, only the chemical viscosity, among the various properties of the chemical, was considered in the correlation of the final spill depth (or area).

The results from both the indoor and outdoor ice spreading experiments were used to obtain a correlation for the final spill area. The result obtained is:

$$h_f \propto V^{0.15} \quad \mu^{0.24}$$

or, in terms of the final spill area;

$$A_f \propto V^{0.85} \quad \mu^{-0.24}$$

where μ is the chemical viscosity, and V is the spill volume. (It was found that the effect of roughness of the ice surface was relatively small. In addition, due to the nature of the interaction between the roughness height and the chemical, which involves the wettability of the chemical on ice and the actual roughness height, both which are often unknown, an "average" of the results for the three surfaces was used for the data correlation.)

The above expression for A_f was non-dimensionalized by introducing the chemical density (ρ_c), liquid surface tension (σ_c) and the gravitational constant, (g), to produce the following equation:

$$\frac{A_f}{V^{2/3}} = K \frac{V^{0.18} \quad \rho_c^{0.33} \; g^{0.21}}{\mu^{0.24} \quad \sigma_c^{0.09}} \qquad (4.1)$$

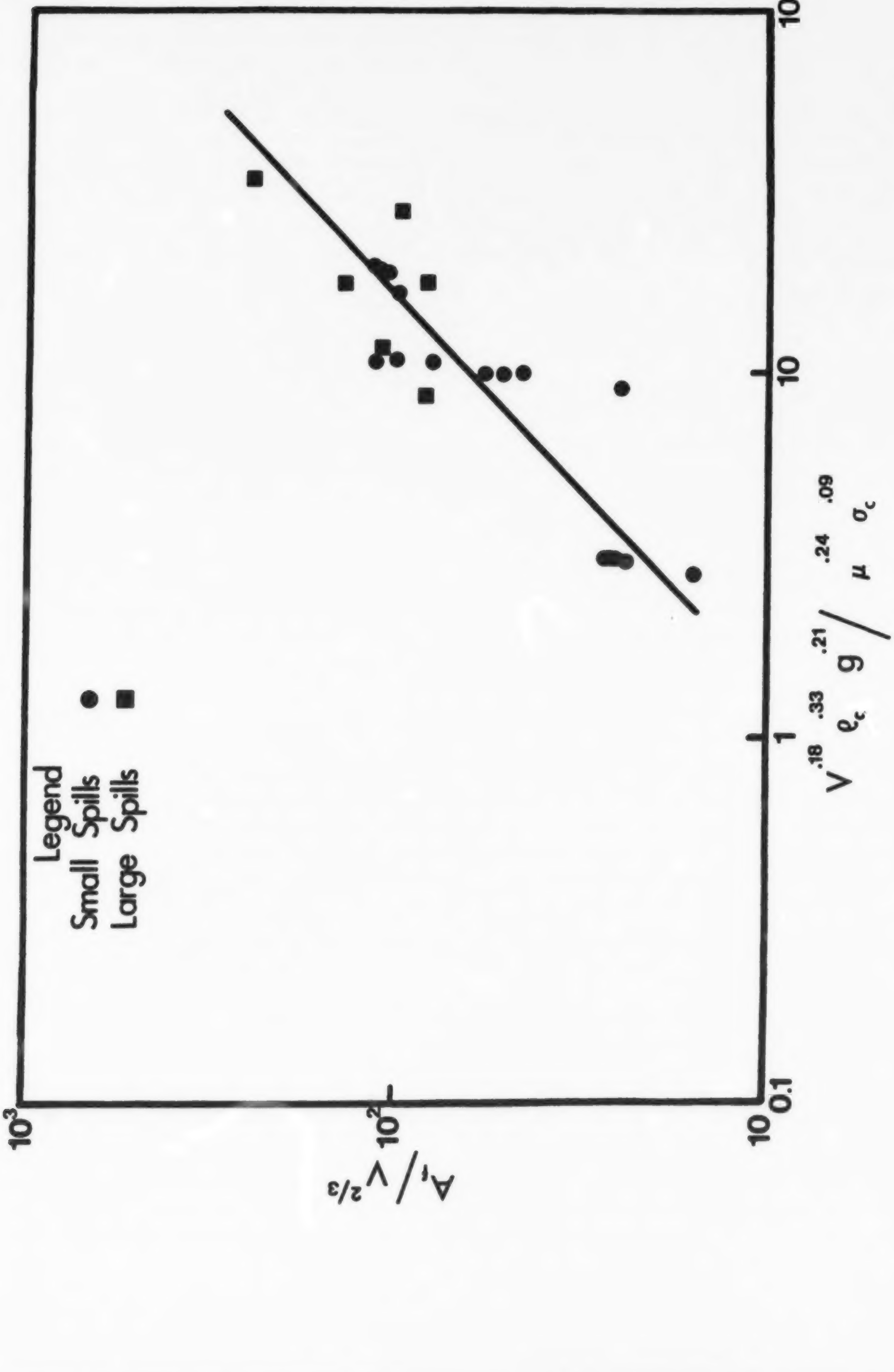
It is important to note that the powers of the chemical density and the liquid surface tension are a result of the non-dimensionalizing process and were not obtained from the results of this study. This does not introduce a serious error because the power on surface tension is small and liquid densities vary over a relatively narrow range. A plot of equation 4.1 and the experimental data is presented in Figure 1. A line with a slope of 1.0 was drawn, and this line was used to determine the constant, K, in equation 4.1. This value was found to be 6.0. Therefore, the final equation for the final spill area can be written as:

$$\frac{A_f}{V^{2/3}} = 6.0 \frac{V^{0.18} \quad \rho_c^{0.33} \; g^{0.21}}{\mu^{0.24} \quad \sigma_c^{0.09}} \qquad (4.2)$$

An algebraically equivalent expression for the final spill depth, h_f, is:

$$h_f = 0.008 \; V^{0.15} \quad \mu^{0.24} \qquad (4.2a)$$

Figure 1: Correlation of Final Spill Area on Ice



where h_f has units of m; V, m^3, and μ, kg/m s. Note that the above correlation is not dimensionless and is dependent on the units used. Since ρ_c and σ_c do not vary greatly for most chemicals, similar results will be obtained by using either equation 4.2 or 4.2a.

It can be seen from Figure 1 that equation 4.2 is able to correlate the experimental data with reasonable accuracy. The two outdoor experiments (light mineral oil and ethylene glycol), in which their results were not used in the development of this correlation also showed good agreement. It is therefore proposed the equations 4.2 and 4.2a (equation 4.2 was developed from the results of 4.2a) can be used to obtain a reasonable estimate of the final spill area for Group 1 and 2 chemicals and with caution for Group 3 chemicals. The difference between the experimental spill areas and the areas predicted by equation 4.2 ranged between 2 and 50%, with an average difference of 23%.

It should be noted that equations 4.2 and 4.2a were correlated from the data obtained under varying wind speeds, and this equation does not explictly include the effect of wind speed in determining the final area. Although quantitative measurements of the wind speeeds were not recorded, it was observed from the outdoor experiments that spreading of low viscosity chemicals, such as xylene (viscosity 0.9 cp), was significantly affected by strong winds.

The effect of similar wind speeds did not influence the spreading of pentanol (11 cp) in comparison with xylene, and had no noticable effect for light mineral oil (450 cp). (The other experiments were performed when the winds were calm.)

Although only a single experiment involving Group 3 chemicals was performed, the assumption that for instantaneous spills, the dissolution process during its relatively short spreading time does not significantly alter the spreading characteristics appeared to hold true. The viscosity of these chemicals can either increase or decrease as a result of dissolution of ice, depending on the relative viscosities of the chemical and water. Yet, when ethylene glycol was discharged, cracking sounds were heard. An inspection of the ice surface at the end of the experiment revealed several cracks in the ice, through which some of the chemical drained. The cracking was most likely due to a temperature drop of the ice surface, induced by the decrease in chemical temperature as a result of absorption of heat required for dissolution of ice. It is thought that the volume increase from ice dissolution was offset somewhat by the loss of chemical through cracks in the ice. It is therefore suggested that caution be exercised when using equation 4.2 for Group 3 chemicals until further experiments are conducted.

4.2.2. Kinetics of Spreading on Ice.

The spill area versus time profiles for the ice spreading experiments were determined from the analysis of the video pictures taken during the experiment.

From these profiles, the spreading time constant, which was defined as the spreading time necessary to reach 63% of the final area, was correlated with the chemical viscosity and spill volume. Again, an average of the time constants for the smooth and rough ice surfaces were used for the correlation.

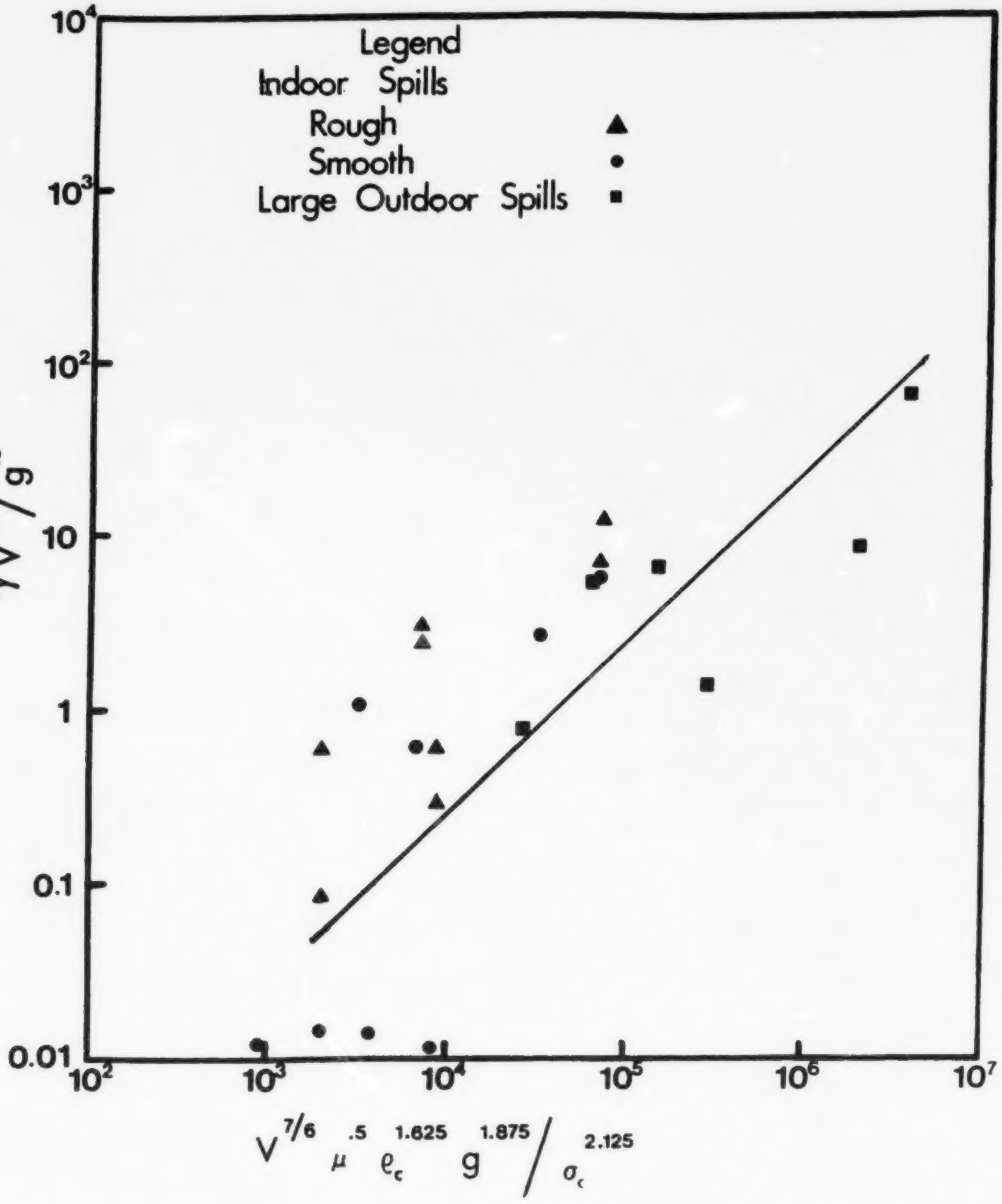
From these results, the following relationship was deduced:

$$\gamma \propto \mu^{0.5} V$$

This was used to produce the following dimensionless equation for the spreading time constant:

$$\frac{\gamma V^{1/6}}{g^{0.5}} = 2.5 \text{ E-05} \; \frac{V^{7/6} \, \mu^{0.5} \, \rho_c^{1.625} \, g^{1.875}}{\sigma_c^{2.125}} \qquad (4.3)$$

Figure 2: Correlation of Ice Spreading Time Constant



The non-dimensionalization, and the constant, 2.5 E-05, was determined as described previously. Equation 4.3 and the experimental data are shown in Figure 2.

A dimensional version can also be written:

$$\gamma = 5\ \mathrm{E{+}05}\ V\ \ \mu^{0.5} \qquad (4.3a)$$

in which γ has units of seconds, V, m^3; and μ , kg/m s. Although the method of discharge, and consequently the spill release rate differed for the small and large ice spreading experiments, this effect was not considered to significantly affect the spreading time constant in these experiments since the discharge time relative to the spill duration was very small in both cases. For the outdoor ice experiments, the ratio of the discharge time to the spreading time varied between 0.002 and 0.01. The actual discharge rates were estimated at values between 200 and 500 mL/s for most experiments.

From Figure 2 it can be seen that the spreading time constants predicted by equations 4.3 and 4.3a can, in extreme cases, overpredict or underpredict the actual time constant by an order of magnitude. Thus, caution should be exercised when applying these equations to determine the spreading rate for actual spills. Unlike the correlations developed to estimate the final spill area, in which the spill rate is not believed to signifcantly affect the extent of spreading, the discharge rate may play a significant role in the spreading time, especially for large volume spills. For example, the spreading duration for a 10,000 L spill, in which the discharge rate is 10 L/s (complete discharge time of 17 minutes) will probalbly be longer than at 100 L/s (2 min. discharge time). Furthermore, if the spill volume is very large at the spill rate small, such that the discharge time is very long, the time of discharge may exceed the spreading duration predicted by equation 4.3 or 4.3a and 4.4. It appears that a more accurate correlation cannot be developed without including effects of chemical-ice interaction, surface roughness, and the spill discharge rate.

The second phase of the spreading kinetics study focused on determining the value of the slope term, x, in equation 2.2. The method involved finding the value of x, using equation 2.2, which best matched the experimental spill area-time profiles for all ice spreading experiments. It was determined that the best value of x ranged between 0.3 and 0.7 for all but on experiment, with 0.5 being the best or next-to-best value for 14 out of the 21 ice experiments.

The only experiment in which the best x value did not fall in this (0.3-0.7) range was the 1 L outdoor xylene experiment, which had a best x of 1.0. This was due to the effect of strong winds, which accelerated the spreading. The effect of wind on the value of x for the higher viscosity chemicals was found to be negligible.

In spite of this result, it is believed that a value of x of 0.5 will adequately describe the kinetics of spreading for most chemicals under most conditions. The time of spreading can be estimated from equation 2.2 (with x = 0.5) by setting the area to be 95% of the final spill area when spreading stops. The spreading time, τ_f, is thus approximately:

$$\tau_f = 9\ \gamma \qquad (4.4)$$

4.3. Spreading on Snow

4.3.1. Spills of Insoluble Chemicals on Snow. Observations from the experiments involving insoluble chemicals (Group 1 and 2) on snow confirmed the expectation that the chemical is readily absorbed by snow and will spread radially along the bottom of the snowcover. The extent of the surface spreading was minimal in most experiments, and its magnitude was found to depend mostly on the compaction of the snow and the chemical's viscosity. An increase in either of these variables resulted in an increase in surface spill area. A cross section of the snow revealed that there is no radial spreading of the chemical before the liquid reaches the bottom.

The data obtained from these experiments were used to correlate the final subsurface spill area and the rate of spreading. For complete details and explanation of results, consult Kawamura and Mackay's spreading report.

4.3.2. Correlation of the Final Spill Area on Snow. The experimental results from the five snow spreading studies were combined to correlate the final bottom spill area with the chemical viscosity and snow properties. The following relationship for A_f in dimensionless form was obtained (by introducing the same variables and employing the same non-dimensionalizing procedure as described in the ice spreading experiments):

$$\frac{A_f}{V^{2/3}} = 0.45 \frac{V^{0.2}\, d^{0.2}\, \rho_c^{0.8675}\, g^{0.4125}\, \mu^{0.05}}{(\varphi \rho_s)^{0.48}\, \sigma_c^{0.4375}} \qquad (4.5)$$

where ρ_s is the density of the snowcover, d is the snow depth and φ is the snow density parameter, which is defined later.

An expression for the equivalent final spill depth in snow is:

$$h_f = 5.3\text{ E-04 } V^{0.13}\, d^{-0.2}\, \mu^{-0.05}\, (\varphi \rho_s)^{0.48}$$

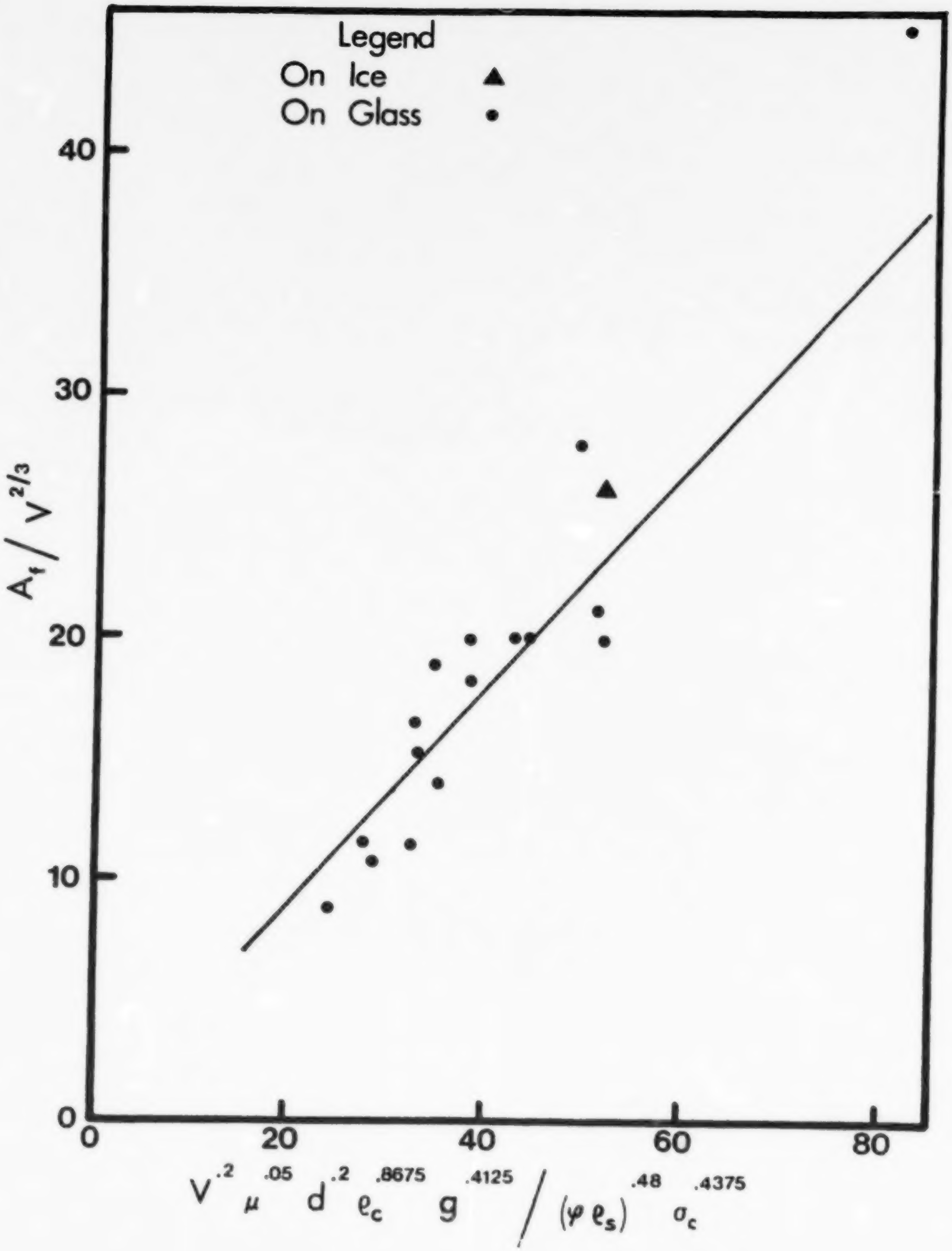
where h_f is in m, V in m^3, d in m, μ in kg/m s, and ρ_s in kg/m^3.

It is worthy to mention that two of the five sets of snow spreading experiments gave unexpected results. The snow depth result revealed that an increase in spill area occurred with increasing snow depths, as reflected in the positive power term for d in equation 4.5. In addition, the chemical viscosity experiments showed a trend of increase in spill area with increasing chemical viscosity. The trend is contrary to what was observed for the experiments on ice surfaces. Several explanations are offered for these results in Kawamura and Mackay (1986).

Although the effect of chemical viscosity on the final spill area is small, the spreading characteristics for highly viscous chemicals, such as heavy mineral oil (1500 cp) was noticably different than for chemicals with lower viscosity. It was observed that the radial surface spreading of mineral oil did not cease until the termination of the discharge onto the snow. In addition, the drainage of the chemical into the snow occurred in "channels", instead of as a saturated front.

The snow density parameter was introduced in this study in the hope that the product of the snow density parameter and the snow bulk density will quantify the properties of the snow which affect the spreading. Specifically, this parameter reflects the degree of resistance to the radial, subsurface spreading of the chemical. The maximum value of 1.0 apply for snow-crystals which still possess some crystalline structure, and this

Figure 3: Correlation of Snow Final Spill Area



offers the greatest resistance to flow. As metamorphic processes, or thaw-freeze cycles convert these crystals to a more or less round shape, the resistance decreases, and is indicated by smaller φ values.

A plot of equation 4.5 and the experimental data is presented in Figure 3. The difference between the experimental spill areas and the areas predicted by equation 4.5 ranged between less than 1% and 29%, with an average difference of 12%. Since this equation was able to correlate the experimental data with reasonable accuracy, it can be used to estimate the final bottom spill area of Group 1 and 2 chemicals.

However, one problem of using equation 4.5 or 4.5a in actual spill conditions is that the snow type and density are usually unknown. (The snow depth, can be measured directly, or obtained from weather stations or estimated from historical data.) Nevertheless, if the age of the snow and the area's overall climate are known, one can make an estimate for the value of these properties. Even if an estimate cannot be made, average or typical values could be employed from Tables 4 and 5.

TABLE 4

SNOW DENSITY PARAMETER

Snow Description	Snow Crystal Type*	φ
Fresh snow, wet or dry (crystalline structure still present)	a,b	1.0
Crusty firn (rounded) snow approx. 1mm in diameter	c	0.5
Advanced firn snow: 2-4 mm in diameter	c,e	0.1

*See Appendix for definitions of snow crystal type

TABLE 5

DENSITIES OF SNOWCOVER (from Gray and Male (1981))

Snow Type	Density (g/mL)
Settling Snow	0.07 - 0.09
Average Wind Toughened Snow	0.28
Hard Wind Slab	0.35
New Firn* Snow	0.4 - 0.55
Advanced Firn Snow	0.55 - 0.65
Thawing Firn Snow	0.6 - 0.7

*Snow consolidated partly into ice.

There are other variables that may be present in the environment which may influence the spreading behaviour, but were not investigated in this study. These include the presence of stratified snow or ice layers, non-horizontal and porous underlying surface, and the long term effect of spills. In the latter situation, the spill may begin to spread after the initial cessation of spreading due to temperature fluctuations and melt down of snow. Despite these uncertainties, the correlations presented in this study are believed to be able to give an order-of-magnitude estimation of the extent of the subsurface spreading of chemicals in snow.

4.3.3. Kinetics of Spreading on Snow. The spreading time constants for all spreading experiments involving Group 1 and 2 chemicals were determined from spill area vs. time profiles. For this study, time zero was taken as the time when the chemical was first observed at the bottom of the snowcover. These time constants were analyzed and correlated, again, in dimensionless form:

$$\frac{\gamma V^{1/6}}{g^{0.5}} = 0.18 \frac{V^{0.62} d^{0.6} \rho_s^{1.1} \mu^{0.78} g^{1.425}}{\rho_c^{0.065} \sigma_c^{1.815}} \qquad (4.6)$$

Equation 4.6 is presented with the experimental data in Figure 4. An equivalent dimensionless version is:

$$\gamma = 5700 V^{0.45} d^{0.6} \rho_s^{1.1} \mu^{0.78} \qquad (4.6a)$$

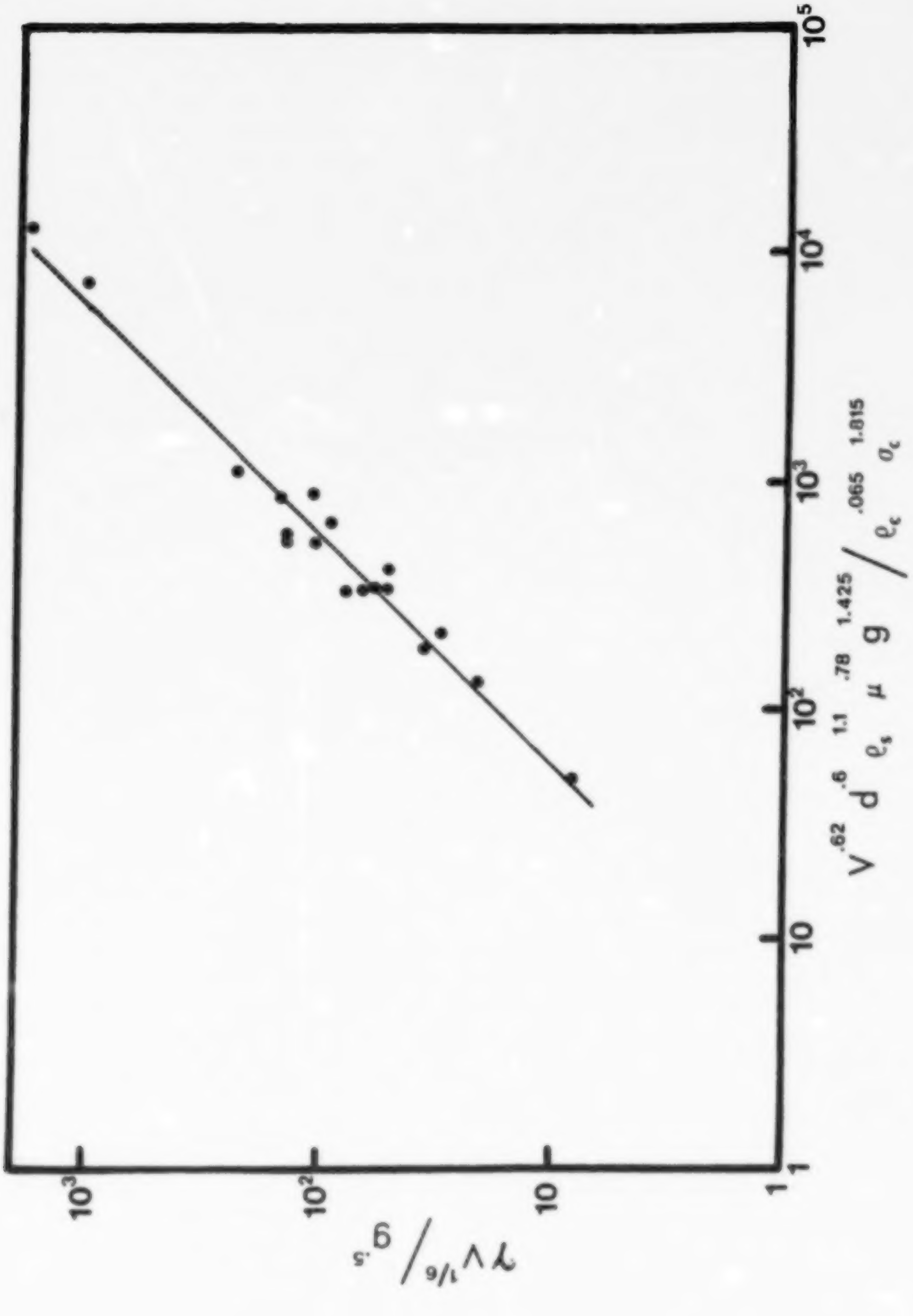
in which γ is in seconds, V in m^3, d in m, μ in kg/m s, and ρ_s in kg/m^3.

Figure 4 shows that equation 4.6 was more successful in correlating the snow experimental spreading time constants than equation 4.3 for the ice time constants. This suggests that the factors which were not studied, but were thought to influence the spreading rates on ice, such as chemical-ice surface interactions are not important for spills on snow surfaces. Therefore, equations 4.6 and 4.6a may be used with more confidence than the corresponding equations for ice surface spills.

It was surprising that the snow density parameter which was required to correlate the spill areas data was not required for the correlation of the time constants. From the results discussed earlier, a decrease in time constant was expected for the experiments involving "lower flow resistance" ($\varphi < 1$) snow crystals. However, close inspection of the experimental area-time profiles revealed that the increase in the rate of spreading was not able to influence the time constants due to the large final areas attained. Since the time constant is the time when the spill area reaches 63% of the now larger final area, the constant was not significantly affected by the type of snow crystal.

As stated previously, an "effective time", which was corrected for the time required for penetration of the chemical to the bottom of the snowcover, was used in the spill area-time profiles to determine and correlate the spreading time constants. There is no doubt that the penetration time can be significant for very viscous chemicals, or for deep snowcover. However, the experimental penetration times were very small in comparison to the spreading time constant or the time of spreading. The experimental ratios of the penetration times with respect to the final spreading times never exceeded 0.06 for all snow experiments. (The average was found to be 0.013.) It was

Figure 4: Correlation of Snow Spreading Time Constant



the result of this calculation and the fact that an accurate prediction of the penetration time would require accurate values of snow depth and properties, which justified the decision to neglect the penetration time in the spreading rate correlation.

The value of x in equation 2.2 was determined using the same procedure employed for the ice experiments. The best value of x for these experiments ranged between 0.5 and 1.0, with an average of 0.75.

The spreading duration can be estimated by equation 2.4. Note that the different value of x for snow, compared to the x value for ice results in a different expression for the spreading time:

$$\tau_f = 4.3\ \gamma \qquad (4.7)$$

4.3.4. Spreading Behaviour of Water Soluble Chemicals. The spill behaviour of water soluble (Group 3) chemicals on snow was observed to be different in many ways, in comparison to Group 1 and 2 spills. Instead of draining through the snow, these chemicals dissolved the snow on contact, with no surface spreading at the discharge area to produce a hole to the bottom of the snowcover. Since the hole was formed almost instantaneously, the time of penetration for these chemicals was very small, ie. of the order of a few seconds.

Immediately after the discharge of chemicals onto the snow, a pool of liquid was observed for all experiments, at the base of the snowcover. A decrease in temperature of the pool of chemical/chemical-snow-slush was observed for all experiments. The maximum temperature depression usually occurred several minutes after the spill and this temperature was maintained until the disappearance of the liquid pool. For the 1 L ethanol spill, the lowest temperature observed was 30°C below the ambient or snow temperature. At this point, continuous measurements of the temperature of the chemical-snow slush revealed that the temperature gradually increased until the termination of the spreading at which the temperature was again approximately equal to the pre-spill temperature.

A cross section of the snow at the end of the experiment, revealed that the chemical did not completely dissolve the snow, and the diluted chemical and snow remained in a slush form at the bottom of the snowcover. A slight "caving in" of the snow at the discharge area was also observed for some experiments. For the spill of ethanol which employed an ice surface under the snow, several large cracks in the ice were observed. The width of these cracks ranged from 1 mm to 5 mm, and the chemical was able to penetrate to the bottom of the 2 cm thick ice cover through these cracks. The cracking is attributed to the rapid decrease in temperature.

The final spill areas attained by Group 3 chemicals in these experiments were found to be much larger (8 to 10 times) then for similar spills of insoluble chemicals as predicted by equation 4.5. A similar comparison can be made for the spreading time constant. The spreading rates and durations for experiments involving ethanol and ethylene glycol were much slower and longer than for Group 1 and 2 chemicals, but sulphuric acid had a much faster rate of spreading.

These observations can be explained in part by the magnitude of the temperature depressions observed in these experiments. This magnitude depends on inter-related factors such as the rate of dissolution of snow and the heat of mixing property of the chemical. Since all Group 3 chemicals will, if given sufficient energy, melt and dissolve an infinite amount of snow and ice, the extent of dissolution and spreading must be heat-transfer-influenced process. The spreading will probably essentially stop when the chemical can no longer draw heat from the surroundings to melt additional snow at an appreciable rate. Since snow is a good insulator, the heat flux is limited. Therefore, under similar spill conditions, the chemical with the highest exothermic heat of mixing is thought to dissolve the greatest amount of snow, and hence, spread the farthest. This was confirmed by the results of this study. Similar arguments can be made to explain the rate of spreading of Group 3 chemicals. A thorough discussion is presented in Kawamura and Mackay's spreading report.

Due to the small number of spreading experiments performed for Group 3 chemicals, no attempt was made to quantify the effects of snow dissolution and heat of mixing on the spreading behaviour.

4.4. Application of this Study to an Actual Spill Situation

It is believed that the results of this study can be used to obtain a reasonable estimate of the general spreading behaviour of chemicals spills on snow and ice surfaces. Since the chemical's ability to dissolve snow/ice is a major parameter affecting the spreading and its behaviour, this property should be determined before any calculations are made. This study recommends a simple, 3-group classification system of chemicals, which can be used to estimate the extent of dissolution.

If a spill occurs on an ice surface, the final spill area and the spreading time constant can be predicted by equations 4.2 or 4.2a and 4.3 or 4.3a. Chemical viscosity and spill volume were found to be the major variables which affect the spreading behaviour. The spreading time constant serves two purposes: it can be used in equation 2.2 with x of 0.5 and the final area from equation 4.2 to obtain a profile of the increase in spill area with time; and it predicts the time spreading, which can be approximated to be the product of a factor of 9 and the spreading time constant. Due to the chemicals selected in these experiments, these correlations apply only for chemicals in which water is not completely soluble (Group 1 and 2 chemicals) but they can be used with caution for water-miscible (Group 3) chemicals. It should also be noted that these correlations break down for low viscosity chemicals, such as xylene (0.9 cp), under high wind speeds.

Since ice is virtually impermeable to Group 1 and 2 chemicals, evaporation is the only natural removal process for these chemicals. For Group 3 chemicals, the chemical may migrate through existing cracks in the ice or cracks formed by the temperature drop associated with the spill of these chemicals. This will be of greatest concern if the spill occurs on ice on underlying body of water.

The spreading behaviour of chemical spills on snow is more complicated than for ice spills. For Group 1 and 2 chemicals, the chemical will be absorbed into the snow and will spread radially along the ground-snow interface. The spreading on the surface of the snow will be relatively small under most conditions. Exceptions may be spills of very viscous chemicals and/or spills on crusty or ice covered snow. The extent and the rate of subsurface spreading in snow media is significantly smaller and slower than for a corresponding spill on an ice surface. This area can be estimated by equation 4.5 or 4.5a and the time constant by 4.6 or 4.6a. The final spreading time can be approximated to be 4.3 times the time constant. The key variables required for these correlations are: chemical viscosity, spill volume, snow depth, density and crystal type. Although specific snow properties are usually now known, typical values could be used.

Equations 4.5, 4.5a, 4.6 and 4.6a are believed to provide a reasonable estimate of the spreading behaviour of Group 1 and 2 chemicals in snow.

However, these correlations are not recommended for a ground surface with a significant slope (ice surface is not a problem since it is usually formed horizontally), and in the presence of highly stratified snow and ice layers.

Spills of Group 3 chemicals are characterized by a "hole" in the snow at the point of discharge. Although the subsurface spreading extent and rate for these chemicals were not quantified explicitly in this study, the final area was found to be significantly greater than predicted by equation 4.5 or 4.5a by a factor of 8 to 10 times. The results of these experiments suggest that the spreading characteristics for these chemicals are controlled by the various heat transfer processes that occur in the chemical-snow system.

5. CONCLUSIONS

5.1. Evaporation

Two models, the "direct evaporation" equation that the "surface temperature" method have been developed, which predict the evaporation rate of pure volatile liquid chemicals resulting from ground spills. The models are relatively simple, based on available physical-chemical data, and include effects of variables such as evaporative cooling, solar insolation, and thermal conduction from the ground. The models are regarded as being applicable to liquids with boiling points in excess of 10° below ambient temperatures.

Evaporation experiments were performed in which the predictions from the two evaporation models were compared with the experimental evaporation rate. The two models showed satisfactory agreement with the experimental evaporation rates. The difference between the model predictions and the experimental evaporation rates for these experiments ranged from 0 to 40% for the direct evaporation model, and 1 to 32% for the surface temperature model.

Although slightly more accurate results were obtained for the surface temperature method, the direct evaporation equation is preferred because of its simplicity and convenience. It is probable that personal preference, and the desired accuracy will dictate which model should be employed in the estimation of the evaporation rate for spill situations.

5.2. Spreading

Spreading behaviour of chemicals on two surfaces, snow and ice, was studied. Spreading experiments were conducted on these surfaces, using various chemicals. It was found that the extent and the rate of the spreading of chemicals on an ice surface is dependent mostly on the spill volume and the chemical viscosity. Under experimental conditions, the time of spreading was in the order of minutes to hours, for most chemicals. For a spill on snow surfaces, the snow depth and its properties were also found to be important. The spreading time in this medium was found to be in the order of hours to days. Furthermore, results of experiments involving water miscible chemicals on ice and snow covered ice surfaces revealed that cracking, and subsequent migration of the chemical through these cracks can occur.

The experimental data, in particular the final spill area (subsurface spill area for snow) and the spreading rates were correlated in both dimensional and dimensionless form. The correlations are believed to be applicable for chemicals in which water is not completely soluble but can be used with caution for water-soluble chemicals for spills on ice.

These correlations form part of the general spreading model which was also developed in this study. The model is relatively simple, and contains terms for evaporation, absorption and snow and ice dissolution.

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APPENDIX

The National Research Council of Canada (1954) has classified snow grain shape into five broad categories:

Class a: Freshly deposited snow, excluding ice pellets, graupel (snow pellet) and hail.
Grain size: <0.5 mm (but crystals size can be as large as 5 mm)

Class b: Settled snow, that has lost most of its crystalline character but fairly soft.
Grain size: 0.5 - 1 mm

Class c: Irregular or rounded grain shape as a result of thaw-freeze cycle. Dull appearance, fairly soft when wet but very hard when frozen.
Grain size: 1 -2 mm

Class d: Irregular shaped grains with facets, as a result of transformation under temperatures well below freezing. Sparkles under sunlight. Almost all of the settled snow in the Arctic falls into this category. Usually fairly hard.
Grain size: 2 -4 mm.

Class e: This snow is termed depth hoar. Hollow cup-shaped crystals. Produced under a long and uninterruped cold period. Found mostly in the lower part of the snowcover.
Grain size: > 4 mm

(The grain sizes quoted above are estimates, and may fall outside of this range, depending on factors such as wind speed, temperature, the type of metamorphic process and external conditions.)

QUANTIFICATION OF FIRE HAZARDS OF LIQUID SPILLS FROM TANK TRUCKS

W.P. Crocker and D.H. Napier
Department of Chemical Engineering and Applied Chemistry
University of Toronto

1.0 INTRODUCTION

A recent study by the Congress of the United States (1) has indicated that in highway transport more accidents, spills, injuries, deaths and property damage are experienced than by either rail or water. In this paper the quantification of fire hazards associated with the bulk transport of liquid by road carrier are considered. Two classes of liquids were studied, viz flammable liquids and liquefied petroleum gases in view of the differing fire hazards that they present. Gasoline is the most common flammable liquid transported by truck tankers (2) and commercial propane is the most common liquefied petroleum gas.

The vehicle configuration chosen in this study is the tractor plus semi-trailer with a payload for liquid of 40,000 kg; the payloads for commercial propane (filled to 85% of nominal capacity) are 17,000, 22,000 and 27,000 kg. The required vehicle configuration is a tandem tractor and tandem semi-trailer (5 axles).

Several fire systems were modelled for each class. Confined and unconfined pool fires were considered for flammable liquids and fireballs were modelled for propane and butane.

Different accident scenarios have been considered from which distances for various levels of thermal radiation and for contact ignition were predicted. Flammable liquid spills of ethanol, gasoline, hexane, kerosene and toluene were compared during this study.

2.0 HAZARD ASPECTS OF TRANSPORTATION OF FUELS

2.1 Cargo Tanks

Within the scope of this paper, structure of truck tanks is important in the context of behaviour on impact.

The main features of the MC306 truck tank used for flammable liquids (vapour pressure < 3 psi) are discussed briefly. The material of construction is primarily aluminum, although some are of stainless steel. The minimum wall thicknesses for shell and head depend on the cross-sectional area of the tank. Low pressure vents must be supplied with the tank, with additional marked venting to prevent pressure buildup in case of fire exposure. The product discharge openings are supplied with emergency valves which close in the event of fire exposure. MC306 cargo tanks are considered non-pressure service (3).

The tank used to transport commercial propane and butane is MC331. The main features of MC331 design (4) are briefly summarized here. Tank construction must conform to the ASME Boiler and Pressure Vessel code. Material of construction must be resistant to brittle failures at temperatures as low as -34°C. There are usually two spring-loaded pressure-relief valves fitted into 8 cm holes in the tank top. These are set at about 1.86 MPa (not greater than 110% Tank Design Pressure). The valves are designed to avoid tank rupture due to pressure buildup.

2.2. Fuel Classification

Flammable liquids and LPG are dangerous commodities as defined by the Transportation of Dangerous Goods Act, 1985. In Table 1 the physical and chemical properties of the selected materials are given. In Table 2 the classification of the fuels considered in this paper are given.

TABLE 1: FUEL PROPERTIES

FUEL	DENSITY ($kg\ m^{-3}$)	ΔH_c ($kJ\ kg^{-1}$)	MW	AVERAGE FLAME TEMP. (K)	NORMAL BOILING PT. (K)	FLASH POINT (K)
Ethanol	794	26800	46.07	1490	351.7	285.9
Gasoline	740	43700		1450	305-498	230.2
Hexane	650	44700	86.18	1300	342.1	242.6
Kerosene	820	43200		1480	424-574	311-345
Toluene	867	42811	92.15	1460	383.8	277.6
Propane	500	50023	44.1	2085	228	Flam.
Butane	600	50213	58.12	1993	271	Gas.

TABLE 2: FUEL CLASSIFICATION

FUEL	UN/NA NUMBER	TDG RATING	TDG CLASS	NFPA FIRE
Ethanol	1170	3.2	Flam Liquid	3
Gasoline	1203	3.1	Flam Liquid	3
Hexane	1208	3.1	Flam Liquid	3
Kerosene	1223/1993	3.3	Flam Liquid	2
Toluene	1294	3.2	Flam Liquid	3
Propane	1978	2.1	Flam Compressed	4
Butane	1011	2.1	Gas	4

2.3 Sources of Ignition

The initiation of a fire requires a source of ignition and the fuel vapour in the flammable range. Ignition sources common in vehicle fires are summarized in the Fire Protection Handbook (5) and include:

1) electrical short circuits causing overheating of conductors
2) sparks from an engine ignition system
3) hot exhaust system

4) overheating of tires, brakes and bearings
5) friction generated sparks from a collision
6) careless use of cigarettes

3. DAMAGE CRITERIA FOR SPECIFYING SAFETY DISTANCES

Two systems are considered in this paper, (1) steady state systems, and (2) time-dependent, non-steady state systems. The damage criteria chosen for hazard assessment depend on the fire system under investigation.

3.1 Steady State Systems

Confined pool fires where the combustion is fully developed are usually steady state systems. Thus intensities of thermal radiation from these fires are used to specify hazard distances. Appropriate values (6,7) are shown in Table 3.

TABLE 3: DAMAGE FROM VARIOUS LEVELS OF THERMAL RADIATION FROM STEADY STATE FIRES

TARGET	RADIATION INTENSITY (kWm^{-2})	EFFECTS
People (Continuous exposure)	1.6	Level of minor discomfort
People	4.7	Threshold of pain Average period for pain to be experienced is 14.5 s
Buildings	12.6	Resins in wood, felt, produce flammable vapours ignitable by pilot ignition
Process Vessel	37.8	Hazardous for process equipment to receive this flux

3.2 Non-Steady State Systems

Unconfined pool fires and fireballs are examples of non-steady state fire systems because the dynamics of the system are dependent on time. In many cases, the fires have a finite duration of combustion and the damage to the environment depends on the thermal radiation dose received by the target. Other systems have time-dependent source terms, causing the size of the fire system to change with time. Obviously, steady state criteria are not meaningful in this case.

Two sets of dose-related criteria were considered here. Values of total radiation dose received during an exposure from transient fires are listed in Table 4 with pertinent physiological effects (8).

TABLE 4: TOTAL DOSE CRITERIA

DOSE THRESHOLD (kJm^{-2})	EFFECT
375	3rd Degree Burns
250	2nd Degree Burns
125	1st Degree Burns
65	Threshold of pain, no blistering observed

The second set of criteria (9) shown in Table 5 related to dosage used in Probit Equations. Dosage, Q_2, is given by

$$Q_2 = \frac{t_e q^{4/3}}{10^4} \quad [s(W/m^2)^{4/3}]/10^4 \qquad (1)$$

where t_e is time of exposure (s)

q steady thermal radiation flux (Wm^{-2})

and when the incident flux is dependent on time, the dosage is given by

$$Q_4 = \frac{1}{10^4} \int_o^{t_e} q^{4/3} dt \qquad (2)$$

where q is radiant flux dependent on time (Wm^{-2})

t_e exposure time (s)

TABLE 5: PROBIT DOSAGES FOR TRANSIENT FIRES

PROBIT DOSAGE	EFFECT
1060	1% Lethality
2300	50% Lethality
210	Blistering of exposed skin
1200	2nd Degree Burns
2600	3rd Degree Burns

4.0 FIRE SYSTEM

Certain aspects of the fire systems have to be determined before the thermal radiation models of the pool fires can be used. These include burning rate, flame length correlations, flame tilt correlations, pool radius correlations for unconfined spills and atmospheric attenuation.

4.1 Atmospheric Attenuation

In practical fire situations, atmospheric attenuation is of importance. The atmosphere surrounding the fire will contain both products of combustion and particulate matter. The intensity of thermal radiation reaching a target will be reduced by these factors.

Attenuation of thermal radiation over the ith band of wavelength is caused by:

i) molecular absorption by the atmosphere - transmissivity τ_{a_i}

ii) scattering by particulate matter - transmissivity τ_{s_i}

The total atmospheric transmissivity is given by summing the effect of the product $\tau_{a_i} \cdot \tau_{s_i}$ over the spectral range under consideration.

Computation of τ has been developed (10) and is based on:

i) calculating τ_{a_i} on the basis of the RH of the atmosphere

ii) determining τ_{s_i} from an empirical relation based on the prevailing value of visual range, V_R. Values of V_R can be allocated by observation as shown in Table 6.

TABLE 6:

VISUAL RANGE (km)	ATMOSPHERIC CONDITION
2	Thin fog (very poor)
5	Haze (poor)
10	Clear (average)
20	Very clear (good)

The attenuated energy distribution is determined using the average wavelength, λ_i, for each window in evaluating τ_{a_i} and τ_{s_i}, consequently, an estimate is made on the total transmissivity, τ_{t_i}, for each window. Energy of the radiation leaving the "attenuated flame" is given by

$$E_{\tau_i} = E_b(\bar{\lambda}) \cdot \tau_{t_i} \qquad (3)$$

and as seen in Figure 4 , the average emissive power of the flame is reduced. The method of calculation of the total transmissivity, τ_t, is, in effect, the ratio of areas under the attenuated energy distribution and the non-attenuated energy distribution; this ratio was estimated by

$$\tau_t = \frac{\sum_{i=1}^{6} E_b(\bar{\lambda}_i)\ \tau_{t_i}\ [\ \lambda_i - \lambda_{i-1}]}{\sum_{i=1}^{6} E_b(\bar{\lambda}_i)\ [\ \lambda_i - \lambda_{i-1}]} \qquad (4)$$

4.2 Burning Rate

The correlation of Burgess and Zabetakis (11), equation (5), was used to estimate the mass burning rate per unit area, $\dot{m}''$ and is given by

$$\dot{m}'' = m_\infty\ (\ 1 - \exp\ [-\ k\beta.D]) \qquad (5)$$

where m_∞ is $1 \times 10^{-3}\ \dfrac{\Delta H_c}{\Delta H_v^*}$ $(kg.m^{-2}s^{-1})$

D pool diameter
$k\beta$ extinction coefficient x mean beam length correction
ΔH_c heat of combustion $(kJ.kg^{-1})$

and $$\Delta H_v^* = \Delta H_v + \int_{T_o}^{T_b} C_p(T)dT \qquad (6)$$

in which ΔH_v is the heat of vaporization at the boiling point $(kJ.kg^{-1})$

T_b normal boiling point (K)
T_o ambient temperature (K)
$C_p(T)$ specific heat $(kJ.kg^{-1}K^{-1})$

Mudan (12) has shown that equation (5) covers a wide range of fuels, including liquefied gases. Values of m_∞ and $k\beta$ are available (13).

Equation (7) due to Babrauskas (13) and based on Blinov and Khudiakov (14), allows estimation of mass burning rate, m_w, when a wind is present.

$$m_w = \dot{m}''\ [\ 1 + 0.15\ V/D] \qquad (7)$$

Equation (7) is not applicable to alcohol and for wind velocities causing flame blow off (i.e. for some fuels, $V > 5\ m.s^{-1}$)

4.3 Flame Length Correlations

The correlation (15), equation (8), was used in this paper.

$$L = 42D \left(\frac{\dot{m}''}{\rho_o \sqrt{gD}} \right) \qquad (8)$$

where L is mean flame length (m)

D pool diameter (m)

ρ_o ambient air density $(\mathrm{kg.m^{-3}})$

$\dot{m}''$ mass burning rate per unit area $(\mathrm{kg.m^{-2}s^{-1}})$

g $9.81\ \mathrm{m.s^{-2}}$

Equation (8) applies to still air; that for windy conditions is given in equation (9) (16).

$$L = 55D \left(\frac{\dot{m}''}{\rho_o \sqrt{gD}} \right)^{0.67} V_*^{0.21} \qquad (9)$$

where V_* is dimensionless wind velocity, $\frac{V}{V_c}$

and V wind velocity $(\mathrm{m.s^{-1}})$

V_c characteristic wind velocity, $\left(\frac{g\, \dot{m}'' D}{\rho_o} \right)^{1/3}$

if $V < V_c$, V_* was assumed equal to unity.

4.4 Flame Tilt Correlation

Wind-engendered tilt has been predicted by using the correlation of Welker and Sliepcevich (17).

$$\frac{\tan\theta}{\cos\theta} = 3.3\ \mathrm{Re}^{0.07}\ \mathrm{Fr}^{0.8} \left(\frac{\rho_g}{\rho_o} \right)^{-0.6} \qquad (10)$$

where Re is Reynolds Number, ie. $\frac{DV\rho_o}{\mu_o}$

Fr Froude Number, ie. $\frac{V^2}{Dg}$

μ_o viscosity of ambient air $(\mathrm{kg.m^{-1}s^{-1}})$

ρ_g density of fuel vapour at normal boiling point $(\mathrm{kg.m^{-3}})$

θ deflection of flame from the vertical

5.0 THERMAL RADIATION MODELS OF POOL FIRES

This section of the paper outlines the details of the thermal radiation models for confined and unconfined pool fires.

5.1 Confined Pool Fires

The size and geometry of the confined pool fire is determined by the shape of the pool. Two common shapes were examined in this paper, viz circular and rectangular.

The circular pool fire is best described as a cylindrical solid flame with a uniformly radiating surface. Prediction of the radiative heat transfer between the flame and the target is based on the Stefan-Boltzmann equation, viz

$$q = F_{f\rightarrow tgt} A_f \, \tau\varepsilon\sigma \, [T_f^{\,4} - T_o^{\,4}] \qquad (11)$$

where q is the incident heat flux at the target ($kW.m^{-2}$)

$F_{f\rightarrow tgt}$ view factor, ie. the fraction of radiation leaving the flame that is incident upon the target

A_f area of the flame "seen" by the target (m^2)

τ atmospheric transmissivity

σ Stefan-Boltzmann constant: 5.676×10^{-11} $kWm^{-2}K^{-4}$

T_o ambient temperature

and

$$\varepsilon = 1 - \exp(-KD) \qquad (12)$$

where ε is flame emissivity

K extinction coefficient (m^{-1})

D pool diameter (m)

At the pool diameters studied, the emissivity has been taken as unity. As shown recently (18) the view factor due to Morgan and Hamilton (19) is most appropriate for an upright cylinder and a vertical target receiver,(Figure 1); it is given by

$$F = \frac{1}{\pi S} \tan^{-1}\left[\frac{L_1}{\sqrt{S^2-1}}\right] +$$

$$\frac{L_1}{\pi}\left[\frac{(A-2S)}{2\sqrt{AB}} \tan^{-1}\sqrt{\frac{A(S-1)}{B(S+1)}} - \frac{1}{S} \tan^{-1}\sqrt{\frac{S-1}{S+1}}\right] \qquad (13)$$

where $R = D/2$

$S = x/R$

$L_1 = L/R$

and $A = (S+1)^2 + L^2$

$B = (S-1)^2 + L^2$

The channel pool fire defined by its aspect ratio, length/width, is shown in Figure 2 . If the aspect ratio is greater than 2, the channel fire model described below is suitable. However, if the aspect ratio is below 2, it is recommended that a hydraulic radius should be used in the circular pool model (20). The pool fire is modelled as an equivalent radiator. Equation (11) is used in conjunction with the view factor given below to predict the incident heat levels at vertical targets at the ground. The flame length is assumed to be twice the width. The applicable view factor (geometry shown in Figure 2). is given by

$$F = \frac{1}{2\pi}\left(\frac{B}{\sqrt{1+B^2}}\tan^{-1}\frac{C}{\sqrt{1+B^2}} + \frac{C}{\sqrt{1+C^2}}\tan^{-1}\frac{B}{\sqrt{1+C^2}}\right) \qquad (14)$$

where $B = \frac{R}{x}$ and $C = \frac{L}{x}$

R, L and x are shown in Figure 2.

F must be doubled to account for the other half of the flame, A_2.

5.2 Flame Tilt Model for Confined Pool Fires

Wind tilts the flame downwind decreasing the separation distance between the flame and the target and creating an impingement hazard in the near field. Quantifying the thermal radiation levels in the direct downwind is possible for the fire system shown in Figure 3. The flame is represented by a tilted cylinder at a flame tilt, θ , and the target has an orientation, β. The view factor, due to Raj (21) is given by

$$F = \frac{1}{\pi}\left[\sin(\theta+\beta)(A_1\cos\phi + hA_2) + (A_3 - A_4)\cos\beta\right] \qquad (15)$$

where θ is angle of tilt

ϕ $\sin^{-1}(1/S)$

h $\frac{\text{flame length in wind}}{\text{pool radius}} = \frac{L}{R}$

S dimensionless distance $= \frac{x}{R}$

and A_1 is given by

$$A_1 = \frac{1}{B_1}\left(\tan^{-1}\left(\frac{h-(S-1/S)\sin\theta}{B_1}\right) + \tan^{-1}\left(\frac{(S-1/S)\sin\theta}{B_1}\right)\right) \qquad (16)$$

where $B_1 = [(S^2-1)\cos^2\theta + (1-1/S^2)\sin^2\theta]^{1/2}$

and A_2 is obtained by

$$A_2 = \int_o^{\pi/2} f(V)\,dV \qquad (17)$$

where $f(V) = \frac{\sin V}{(1+h^2+S^2-2Sh\sin\theta) + 2(h\sin\theta - S)\sin V}$

5.3 Unconfined Pool Fires

Modelling of unconfined pool fires depends on the actual spill scenario chosen. In the paper, Mudan's (12) classification based on the rate of release and duration of the spill will be used. Three categories include:

(1) Instantaneous spills - in which all of the spill occurs in a very short time.
(2) Continuous spills - in which the spill continues at a specified finite rate for a "long time".
(3) Quasi-continuous spill - where a given volume of liquid is spilled over a given duration of time. This rate of release is finite, but can vary with time.

The approach and assumption made in the modelling for each category will be explained in the following sections.

5.3.1 Instantaneous Spills. Modelling an instantaneous release (ie. from a catastrophic tank failure) of liquid requires an expression to predict the spreading and burning of the liquid. Raj (21) developed equation (18) in which the following assumptions were made:

(1) spill surface is impermeable
(2) spill surface is flat and smooth, and
(3) constant evaporation rate.

The expression to predict the radius of the spreading pool fire, R(t), at any time, t , is

$$\left(\frac{R(t)}{R_m}\right)^2 = \frac{\sqrt{3}}{2}\left(\frac{t}{t_m}\right)\left[1 + \left(\frac{2}{\sqrt{3}} - 1\right)\left(\frac{t}{t_m}\right)^2\right] \tag{18}$$

and

$$R_m = \left[\frac{V^3 g}{Y^2}\right]^{1/8} \tag{19}$$

where R_m is maximum pool radius (m)
Y regression rate (m/s)
V volume of liquid spilled (m³)

and

$$t_m = 0.6743\left[\frac{V}{gY^2}\right]^{1/4} \tag{20}$$

where t_m is time to reach maximum radius (s)

Unconfined pool fires are time-dependent. The development of the thermal radiation models of unconfined pool fires involves a quasi-steady state analysis. This allows the use of equations derived from steady state conditions in the unsteady state system of the unconfined pool fire.

The approaches in the modelling were based on two recommendations due to Mudan (12) and Moorhouse (22). The recommendations and the model development are detailed in the following sections.

Mudan Model

This model involves the use of a time-averaged pool diameter obtained by integrating equation (18) according to

$$\bar{D} = 2 \times \bar{R} = \frac{2}{t_m} \int_o^{t_m} R(t)dt \qquad (21)$$

$\bar{D}$ is shown in model geometry (Figure 5).

However, the thermal radiation hazard is best described by using the dosage received at the target during the pool burning period, t_m. The dose, Q_1, received at the target at position, x , outside the maximum pool radius is given by

$$Q_1 = \varepsilon \sigma T_f^4 \tau(x_p) F(\bar{D},\bar{L},x) t_m \qquad (22)$$

where $F(\bar{D}, \bar{L}, x)$ is the time-averaged view factor

$\tau(x_p)$ atmospheric transmissivity

in which x_p is path length between flame and target, ie. $x_p = x - R(t)$

Two cases were considered for the transmissivity, i.e. no attenuation and vid.4.1

The probit version of this model requires an alternate equation to estimate the dosage, Q_2 , at the target, eg. using equation (2) gives

$$Q_2 = \frac{1}{10^4} \left[\varepsilon \sigma T_f^4 \tau (x_p) F (\bar{D}, \bar{L}, x) \right]^{4/3} t_m \qquad (23)$$

where Q_2 is probit dosage.

Time-Dependent Model

A more detailed model of this system is obtained by integrating the total radiation dose received by the target during the total burning period of the unconfined pool fire as described by equation (24). The assumption is made that steady state flame length correlations apply to the expanding pool diameters over the total burning period of the fire (22). The dose, Q_3, received at the target is given by

$$Q_3 = \int_o^{t_m} \varepsilon \sigma T_f^4 F [D(t), L(t), x] \tau(x_p) dt \qquad (24)$$

where $F [D(t), L(t), x]$ is the time-dependent view factor

$D(t)$	pool diameter at time t
$L(t)$	flame length at time t
$\tau(x_p)$	atmospheric transmissivity for a path length, x_p

The dose, Q_3, incorporating equations (8,18)) was determined by numerical integration of equation (24). Model geometry is shown in Figure 6.

The probit version of this model is

$$Q_4 = \frac{1}{10^4} \int_0^{t_m} q^{4/3} \, dt \qquad (25)$$

where $q = \varepsilon \sigma T_f^4 F [D(t), L(t), x] \tau(x_p)$

5.3.2 Quasi-Continuous Spills

Instantaneous spills of flammable liquids offer the maximum possible hazard from the road tanker. However, most accident scenarios involve a breach of containment with the liquid leaking out at some time-varying flowrate. The system modelled for this class of spill was based on an MC306 (DOT) truck tanker which experienced a collision at the truck side.

The following assumptions were made regarding the dent size and the hole geometry.

(1) the maximum deflection of the tank shell is set by the location of the chassis
(2) length of the hole was one half the length of the dent
(3) the shape of the hole is elliptical, the width of which is one-eighth the hole length
(4) the tank is upright after the collision.

Frequently tanks roll over and the pattern of drainage differs from that discussed above. This case will not be treated in this paper in that it is a simpler, i.e. one step, drainage which, in the limit, involves a steady flow through a breach of constant size under a progressively diminishing hydrostatic head.

The development of the quasi-continuous unconfined pool fire model involved determining the time-varying discharge rate through the idealized breach in the tanker wall following the method of Oliverio (23). This discharge model provides the source term for a spill fire whose growth is described by a mass balance developed by Cline and Koenig (24). The details of each model are described next.

Discharge Model

Source term development predicting the liquid flowrate through the breach involved application of the Bernoulli Equation to estimate average flow velocity at the hole. Equal decreases in the liquid level permitted estimation of the time interval for the decrease from an overall mass balance on the tank. Two regions in the liquid level were considered during model development, viz liquid above/below the breach. Details for each region are given below.

Liquid level above hole

When the liquid level is above the hole, the discharge area is constant. The head, h_E, of liquid is given by

$$h_E = x_L - \tfrac{1}{2}OD \qquad (26)$$

where x_L is the liquid level measured from the tank bottom (m)
OD the tank depth (m)

and the area of the hole, A_h, is given by

$$A_h = \frac{\pi}{32} H_h{}^2 \qquad (27)$$

where H_h is the hole length (m)

Equations 26 and 27 are used in the Bernoulli Equation to estimate the discharge flowrate, Q, at a head, h_E. The time history of the flowrate when the level drops to the top of the hole was determined by dividing the initial height of liquid above the hole into n parts. Equal drops in the liquid level were then calculated. The time taken for the liquid level to drop to x_{L_i} is estimated by

$$t_i = \sum_{j=1}^{i} \Delta t_j \qquad (i=1,2,...n) \qquad (28)$$

and the flowrate, Q, is taken at the midpoint of the interval, Δt_i, the time of which is defined by

$$\overline{t}_i = t_{i-1} + \tfrac{1}{2}\Delta t_i \qquad (29)$$

Liquid level below hole

As the liquid drops below the hole, the discharge area decreases with time, this feature is shown in Figure 7a. The effective area of the breach is given by

$$A(x) = 2\,\frac{b}{a}\left(\frac{x\sqrt{a^2-x}}{2} + \frac{a^2}{2}\sin^{-1}\frac{x}{a} + \frac{\pi a^2}{4}\right) \qquad (30)$$

where $x = Z - a$
$a = \tfrac{1}{2}H_h$
$b = \tfrac{1}{2}W_h$
and $Z = x_L - H_B$ (31)

where H_B is height of hole bottom (m)
W_h maximum breach width (m)

As the observed level, Z, drops lower, the effective head h_E becomes equal to

$$h_E = \tfrac{1}{2}Z \qquad (32)$$

A similar approach used in the first liquid level regime was taken by dividing the number of decrements, n, over the breach length, H_h, thus the liquid drop, Δh_2, is given by

$$\Delta h_2 = \frac{H_h}{n} \qquad (33)$$

but when the liquid level is at x_{L_i}, the flowrate, Q, over the ith drop is given by

$$Q = C_D A(x)\sqrt{2g\,h_E} \qquad (m^3 s^{-1}) \qquad (34)$$

The flow ceases when h_E is zero. Model geometry is shown in Figure 7b.

Spill Fire Growth Model

Cline and Koenig (24) developed a model to describe the transient growth of an unconfined pool fire. A mass balance on the system illustrated in Figure 8 gives

$$\frac{d}{dt}\left(\begin{array}{l}\text{mass of fuel}\\ \text{in pool}\end{array}\right) = \begin{array}{l}\text{rate of fuel}\\ \text{supplied}\end{array} - \begin{array}{l}\text{rate of fuel}\\ \text{depletion}\end{array}$$

where rate of fuel supplied is the source term from the MC306 tanker

$$\begin{array}{l}\text{rate of fuel}\\ \text{depletion}\end{array} = \begin{array}{l}\text{rate of fuel}\\ \text{burned}\end{array} + \begin{array}{l}\text{rate of fuel}\\ \text{absorbed by ground}\end{array} + \begin{array}{l}\text{pre-burning in}\\ \text{the fuel stream}\end{array}$$

Neglecting the last two terms, the following relationship arises

$$\frac{d}{dt}\left[2\pi\int_0^{R_p}\int_0^{\delta}\cdot\rho_f r\,dz\,dr\right] = \int_A \rho_f V\,dA - 2\pi\int_0^{R_p}\rho_f Y r\,dr \qquad (35)$$

where

R_p	is pool radius at any time after the onset of the fuel release
δ	uniform pool depth during spreading
ρ_f	fuel density
r	radial coordinate of volume element
z	vertical coordinate
A	effective rupture area
V	transient discharge velocity
Y	surface regression rate for the flammable liquid.

The general solution becomes

$$y = \frac{\exp\left[\frac{-Yt}{\delta}\right]}{\pi\delta}\int_0^t \exp\left[\frac{Yt}{\delta}\right] Q(t)\,dt \qquad (36)$$

where Q(t) is the volumetric flowrate dependent on time $(m^3 s^{-1})$

Determination of the pool radius, R_p, as a function of time requires the knowledge of the discharge function, Q(t), from the numerical discharge model. The time intervals from the discharge model are uneven because equal drops in the liquid level were chosen. The area underneath the integrand function in equation (36) was approximated by the Mid-point Rule (Rectangles). The numerical solution of equation (36) becomes

$$R_p{}^2 = \frac{\exp\left[\frac{-Y\bar{t}_j}{\delta}\right]}{\pi\delta} \left(\sum_{j=1}^{i} \exp\left(\frac{Y\bar{t}_j}{\delta}\right) Q(\bar{t}_j) \Delta t_j \right) \qquad (37)$$

where $\Delta t_j = t_j - t_{j-1}$

$\bar{t}_j = t_{j-1} + \frac{1}{2}\Delta t_j$

Isothermal Time-Dependent Fireball Model

The model for isothermal fireballs developed by Lihou and Maund (25) was modified to incorporate the dynamics of the rising and expanding fireball. Equations of the modified model enabled the prediction of thermal radiation dosage and consequently of different levels of personal injury. Atmospheric attenuation was incorporated into this model. The entire mass is assumed to be burning at an isothermal temperature (T_c). Model is shown in Figure 9. The initial D_o, and the final diameter, D_c, are estimated from

$$D_o = 0.539 \left(\frac{T_o m}{M}\right)^{1/3} \qquad (38)$$

$$D_c = 0.539 \, [\nu + (n+1)f_c]^{1/3} \left(\frac{T_c m}{M}\right)^{1/3} \qquad (39)$$

where m is mass of fuel in cloud (kg)

M molecular weight

ν stoichiometric molar ratio of air to flammable gas

n increase in total number of moles per mole of gas burned

T_o ambient temperature (K)

f_c fraction of fuel cracked (chosen as 0.95)

and accounting for volume expansion, the diameter increases at a rate of 10.7 ms^{-1}. Neglecting time to lift-off, the time to complete combustion, t_c, is estimated by

$$t_c = \frac{D_c - D_o}{10.7} \qquad (40)$$

Prediction of the fireball diameter at any time, t, is necessary to evaluate the dose. The fireball diameter was estimated by linear interpolation.

The elevation of the fireball, H, at time, t, is

$$H = 10t \tag{41}$$

where H is fireball elevation measured from fireball bottom (m)

Isothermal temperatures for the fireball can be estimated by heat and mass balance correlations (25). In an ambient temperature of 21°C, isothermal temperatures for propane and butane fireballs are shown in Table 1. (26,25)

The radiation flux, q, incident at the vertical ground target is

$$q = \varepsilon\sigma F(t)\ T_c^{\,4} \tag{42}$$

and F(t), the view factor, is given by

$$F(t) = \left(\frac{R(t)}{S}\right)^2 \frac{x}{S} \tag{43}$$

$$R(t) = \frac{D(t)}{2}$$

$$S^2 = [R(t) + 10t]^2 + x^2 \tag{44}$$

where R(t) is fireball radius at time, t (m)

x target position, (m)

S distance between target and fireball centre (m)

6. DISCUSSION

6.1 General Limitations in Fire Modelling

(1) Heat transfer is predicted for fully developed fires only.
(2) Models invoke steady state combustion which does not occur either on micro- or macroscale.
(3) There is dependency on small scale experimentation eg. the following are affected thereby: flame temperature (27)
    emissive power
    flame length
(4) There is spatial variation of transmissivity (28).
(5) Models are applicable to "free" fields (20,28).
(6) Ideally, models should incorporate all aspects of fuel type and storage, so that account is taken of both source terms and burning criteria.
(7) Wind effects are incorporated in relation to tilt but little account is taken of differences in the combustion system.
(8) No account is taken of the nature and the environs of the target, eg. damage criteria and absorptivity.
(9) Existing models do not incorporate time-dependency of the fire and of the exposure at the target.

Confined Pool Fires

Hazard distances (vid. Table 7) determined for different flammable liquid pools (10 to 40 m diameter) show great variation in prediction depending on fuel type and pool diameter. Figure 10 illustrates the radiation profiles for ethanol, gasoline and hexane (10 m diameter). Radiation intensities received at the target are dependent on flame temperature and the flame length. Ethanol has the highest near field intensities (highest flame temperature) but they decay rapidly in the far field (shorter flame length). Gasoline radiation levels are received in the far field, due to higher flame lengths although the flame temperature is less than ethanol.

Normalized hazard distance, viz. hazard distance/pool diameter, are dependent on the radiation intensity and the pool diameter for a specific fuel. Figure 11 shows the decreasing trend of normalized hazard distance with pool diameter for gasoline pool fires.

Wind-engendered flame tilt causes significantly higher radiation levels in the near field. This is shown in Figure 12 for a 40 m gasoline pool fire (0, 4 ms^{-1} wind). Reduced injury-hazard distances were observed because in the far field the projected flame length was less than flame length in a quiescent atmosphere. Hazard distances are presented in Table 11 for ethanol, gasoline, hexane and toluene.

Toluene generated the greatest impingement hazard range and ethanol the least. Table 12 lists these ranges for various fuels; the effect of wind is also shown.

Shape of the pool affects hazard distances. Results are presented in Table 9 for a channel fire (aspect ratio, 8 and area equivalent to a 40 m diameter pool). Ethanol channel fires have the greatest hazard distance; those of hexane have the smallest distances. Predictions were based on flame temperatures.

Incorporation of atmospheric attenuation into the model improves the radiation prediction. Hazard distances predicted for 40 m pool fires are shown in Table 8. For gasoline, kerosene, hexane and toluene, the resultant reduction in the hazard distances was up to 20%; this effect is shown in Figure 13. Dependency of intensity on path length is strong in the near field. In Figure 13 significant difference in radiation intensity is not observed until the target is moved away from the flame. The preferred choice for path length is the distance between the target and the midpoint at the adjacent flame front.

Unconfined Pool Fires (Catastrophic Failure)

Two modelling approaches, viz. time-averaged and time-dependent, were used in the prediction of hazard from the ignition of 40,000 kg liquid spilled. Unconfined pool fire properties are listed in Table 13; the maximum pool radii obtained are given for different fuels. Hence ethanol has the largest range of contact ignition of the fuels spilled.

Radiation predictions based on the total dose received at the target were more conservative than those based on the probit dosage. Values obtained from models are given in Table 15 and 16 (Time-averaged version) and in Tables 17 and 18 (Time-dependent version). The latter table for each model is based on probit dosage (5.3.2). Dosage profiles (Time-dependent) are shown in Figure 14.

It may be concluded that the model (equations 23,24) indicates ethanol is the most hazardous fuel. This seems contrary to experience. Care must be exercised in selecting the appropriate values of critical parameters in the system to ensure that realistic levels of radiation, dose and exposure are used. The other fuels which are prone to soot formation (continuum radiation), exhibit blackbody radiation at smaller pool diameters than for ethanol (27). Development of models for different fuels is dependent on well-organized, large scale experimentation to generate data on radiation from flames.

Toluene and gasoline have similar hazard distances for the different burn categories (dose). Kerosene exhibited slightly higher hazard distances due to longer burning times (increasing dosage). Hexane was the least hazardous of the fuels. Comparison of model predictions based on equations (23,24) showed that incorporation of pool growth in the later stages of burning gives 5% greater hazard distances than the time-averaged model. This offers a slight increase in accuracy.

Damage to buildings was studied using the time-averaged model and steady state damage correlations (30). Ranges of ignition hazard were up to 129.5 m (spontaneous ignition) and up to 175.5 m (pilot ignition) for kerosene. Hexane presented the least hazard to buildings (vid. Table 14).

Quasi-Continuous Spills

Ethanol leaking from an MC306 tanker was modelled (regression rate was similar to fuel, JP4, used in the Cline/Koenig model). Figure 15 shows the discharge profile for 38.7 m^3 spilled from the tank. Spill fire growth (shown in Figure 16 reached a maximum radius at 107 m. Estimate of consequence involves assuming a suitable exposure time at the maximum pool diameter and determining the dosage received at the target.

Application of the Cline/Koenig model to large scale systems is not recommended. The model constraint of constant pool thickness, δ, introduced scaling problems. Extrapolation of the model to other fuels was not possible because values of δ were not given. In light of the model limitations, a new model for this system is being developed by the authors.

Fireball Formation

Hazard distances are presented in Tables 20 and 21 for butane and propane (17,22 and 27 tonnes transported) based on total dosage and probit dosage respectively. The fireball formed after catastrophic failure of the MC331 tanker and subsequent ignition of the vapour cloud formed from the adiabatic flashing of the spilled liquid. Liquid entrainment was accounted for by doubling the vapour flash fraction. The model predicted the dosage received by a ground vertical target as the fireball rose above the ground until burnout.

Results indicated that propane is more hazardous than butane. This is due to longer burning times, higher flame temperatures and higher fuel masses in the cloud for an equivalent mass spilled. Table 19 lists the fireball parameters. Figures 17 and 18 illustrate the radiation profiles for propane (17 and 27 tonnes spilled) and the contrast between butane and propane (27 tonnes mass spilled).

7. CONCLUSIONS

In this paper models of thermal radiation of fires have been described including their limitations. Significant findings from this study are summarized below.

1. For confined pool fires, toluene is the most hazardous of the fuels considered (1.6 kWm^{-2} received at 306 m from 40 m pool). Ethanol presented the least hazard.

2. Atmospheric attenuation caused reductions up to 20% (confined pool fire) in the hazard distances predicted.

3. Flame tilt reduced hazard distances for people in the far field (4.7 and 1.6 kWm^{-2}) in confined pool fire systems.

4. Toluene has the greatest range of impingement (eg. 22 m for 40 m pool diameter for 4 ms^{-1} wind).

5. Ethanol represents the greatest contact ignition hazard from catastrophic failure of tank contents (175 m for 40,000 kg spilled).

6. Buildings are in hazard from unconfined pool fires (catastrophic failure), eg. 176 m from pool center for kerosene based on spontaneous ignition.

7. Total dosage criteria give more conservative hazard distances than those based on probit dosage for time-dependent systems.

8. Maximum radius for 1% lethality, is 318 m for kerosene (40,000 kg spilled). Radius for blistering of skin is 553 m.

9. Propane is more hazardous than butane. The distance to the pain threshold for C_3H_8 is 487.6 m for 27 tonnes released; 278 m for C_4H_{10}.

Models for confined and unconfined pool fires (catastrophic failure) are suitable for use in hazard assessment. Work is required to improve the modelling of the quasi-continuous spill fire systems. Incorporation of suitable flame measurements based on fire size or better understanding of scaling laws will greatly improve the accuracy of the fire models.

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NOMENCLATURE

A	view factor (13) parameter
A_f	area of flame "seen" by target (m^2)
A_1, A_2	view factor (15) parameters
A_h	area of breach (m^2)
A(x)	area of breach (level below hole)
B	view factor (13) and (14) parameter
$C_p(t)$	specific heat ($kJ.kg^{-1}K^{-1}$)
C	view factor (14) parameter
C_D	discharge coefficient (chosen as 0.60)
D	pool diameter (m)
$\bar{D}$	time-averaged pool diameter (m)
D_o	initial fireball diameter (m)
D_c	final fireball diameter (m)
D(t)	time-dependent pool diameter (m)
$E_b(\lambda)$	energy of radiation at wavelength, λ
E_{τ_i}	energy of radiation leaving 'attenuated' flame
F	view factor
H_B	height of hole bottom (m)
H	elevation of fireball bottom (m)
h_E	head of liquid (m)
ΔH_c	net heat of combustion ($kJ.kg^{-1}$)
ΔH_v	head of vaporization ($kJ.kg^{-1}$)
ΔH_v^*	modified head of vaporization ($kJ.kg^{-1}$)
h	flame length in wind/pool radius
Δh	decrease in liquid level (m)
L	mean flame length (m)
L_1	flame length/source radius
$\bar{L}$	time-averaged flame length (m)
L(t)	time-dependent flame length (m)
MW	molecular weight
$\dot{m}''$	mass burning rate per unit area ($kg.m^{-2}s^{-1}$)
m	mass of fuel in fireball (kg)
m_w	mass burning rate (wind) ($kg.m^{-2}s^{-1}$)
Q_2	steady state probit dosage
Q_4	time-dependent probit dosage

Q_3	total dose received $(kJ.m^{-2})$
q	radiation intensity at target $(kW.m^{-2})$
Q	discharge flowrate (m^3s^{-1})
R_m	maximum pool radius (m)
$R(t)$	time-dependent pool radius (m)
R_p	pool radius with constant thickness (m)
S	distance from fireball center to target (m)
S	target position/pool radius
T_b	normal boiling point (K)
T_f	flame temperature (K)
T_c	isothermal fireball temperature (K)
t_m	time to reach maximum pool radius (s)
$\bar{t}_i$	average time for ith level decrease (s)
Δt_i	time interval for ith level decrease (s)
t_c	time to complete combustion (s)
V	volume of liquid spilled (m^3)
V	wind velocity (ms^{-1})
V_*	dimensionless wind velocity
V_c	characteristic wind velocity (ms^{-1})
V_R	visual range
w_h	maximum width of breach (m)
x_L	liquid level in tank (m)
x_p	path length (m)
x	target position from source center (m)
Y	regression rate (ms^{-1})
Z	observed liquid level in breach (m)

GREEK SYMBOLS

β	target orientation
δ	constant pool thickness
ε	flame emissivity
ϕ	$\sin^{-1}(1/S)$
λ	wavelength
ρ	density $(kg.m^{-3})$
τ	atmospheric transmissivity
σ	Stefan-Boltzmann constant
θ	deflection of flame from the vertical (flame tilt)

TABLE 7: CONFINED POOL FIRES
Quiescent Atmosphere
50% Relative Humidity
294K (21°C) Ambient Temperature
SRD τ Option
Confined Circular Poolfire
Thomas Flame Length Correlation

R.I.	DISTANCE TO RADIATION INTENSITY (R.I.)			
(kWm^{-2})	10 m	20 m	30 m	40 m
ETHANOL				
37.8	13.7	25.3	36.1	46.6
12.6	24.0	43.0	60.4	76.9
4.7	38.3	67.7	94.5	119.7
1.6	63.3	111.2	154.5	195.1
GASOLINE				
37.8	12.3	25.6	37.9	49.7
12.6	30.1	54.3	76.5	97.5
4.7	50.8	89.8	125.3	158.6
1.6	85.9	150.6	208.9	263.8
HEXANE				
37.8	-	12.1	18.2	24.8
12.6	23.4	43.3	61.8	79.4
4.7	43.0	76.6	107.2	136.0
1.6	74.5	130.9	181.9	229.7
KEROSENE				
37.8	14.5	27.8	40.2	52.1
12.6	29.5	52.8	74.3	94.5
4.7	48.6	85.8	119.6	151.2
1.6	81.4	142.8	198.3	250.1
TOLUENE				
37.8	6.7	21.2	35.2	47.9
12.6	33.4	60.6	85.6	109.2
4.7	58.3	103.2	144.1	182.0
1.6	99.7	175.0	242.0	306.2

TABLE 8: CONFINED POOL FIRES
EFFECT OF ATMOSPHERIC TRANSMISSIVITY ON HAZARD DISTANCES

System: 40 m diameter Pool Fire
Quiescent Atmosphere
Thomas L.
Comparison Between No Attenuation and SRD τ Option

R.I.	Hazard Distance (m)		% Reduction
(kWm^{-2})	$\tau=1$	$\tau<1$	$= \frac{x(\tau=1)-x(\tau<1)}{x(\tau=1)} \times 100\%$
ETHANOL			
37.8	51.1	46.6	8.8
12.6	87.0	76.9	11.6
4.7	139.2	119.7	14.0
1.6	234.5	195.1	16.8
GASOLINE			
37.8	58.7	49.7	15.3
12.6	114.3	97.5	14.7
4.7	190.1	158.6	16.6
1.6	325.7	263.9	18.9
KEROSENE			
37.8	59.6	52.1	12.6
12.6	109.6	94.5	13.8
4.7	179.8	151.2	15.9
1.6	306.5	250.1	18.4
HEXANE			
37.8	28.2	24.8	12.1
12.6	95.4	79.4	16.8
4.7	164.8	136.0	17.5
1.6	285.5	229.7	19.5
TOLUENE			
37.8	61.0	47.9	21.5
12.6	130.7	109.2	16.4
4.7	221.5	182.0	17.8
1.6	382.3	306.2	19.9

TABLE 9: CHANNEL POOL FIRE

Pool Dimensions: 101.3 m x 12.5 m
Flame Height: 25 m
Aspect Ratio: Length/Width = 8
Quiescent Atmosphere/ No Attenuation

R.I. (kWm^{-2})	ETHANOL	GASOLINE	KEROSENE	HEXANE	TOLUENE
37.8	63.0	57.9	61.6	39.5	59.1
12.6	125.8	117.7	123.4	90.9	119.6
4.7	214.3	201.5	210.3	159.7	204.4
1.6	373.0	351.0	366.0	280.9	356.0

TABLE 10: EFFECT OF WIND ON FLAME PROPERTIES
Ambient Temp: 300K

	WIND VELOCITY m/s	FLAME L(m) 20 m	L (m) 40 m	FLAME TILT(°) 20 m	θ (°) 40 m
Ethanol	0	11.7	18.9	0	0
	2	11.1	16.8	18.1	11.5
	4	12.9	19.5	40.0	29.8
Gasoline	0	25.9	41.9	0	0
	2	24.6	38.9	13.9	8.7
	4	28.1	42.5	34.0	24.2
Hexane	0	31.1	50.3	0	0
	2	30.1	47.7	12.8	7.9
	4	33.6	50.9	32.1	22.4
Toluene	0	35.2	56.9	0	0
	2	34.3	54.5	13.1	8.1
	4	37.9	57.3	32.5	22.9

TABLE 11: EFFECT OF WIND ON HAZARD DISTANCES
Thomas L Correlation
No Atmospheric Attenuation
Ambient Temperature: 300K

		POOL DIA. 20 m			POOL DIA. 40 m		
	V R.I.	0 m/s	2 m/s	4 m/s	0 m/s	2 m/s	4 m/s
Ethanol	37.8	27.4	27.9	31.5	51.3	49.3	54.9
	12.6	47.7	45.1	48.0	87.2	79.1	85.1
	4.7	77.1	70.1	71.9	139.8	123.0	129.4
	1.6	130.4	115.6	115.7	235.6	203.1	210.4
Gasoline	37.8	29.7	33.2	40.2	58.6	60.0	68.5
	12.6	62.3	60.3	67.7	114.7	107.1	116.4
	4.7	105.1	97.0	103.9	190.9	172.4	181.9
	1.6	181.0	162.2	168.3	327.2	289.6	299.3
Hexane	37.8	11.9	24.5	29.7	27.5	46.0	52.9
	12.6	50.8	51.8	59.9	95.5	92.4	102.1
	4.7	90.5	86.1	94.0	165.3	152.7	162.5
	1.6	158.0	145.2	152.0	286.6	258.2	267.6
Toluene	37.8	28.3	36.3	44.3	60.6	66.0	75.7
	12.6	70.8	70.2	79.0	131.1	124.5	134.9
	4.7	122.3	115.1	122.9	222.4	204.0	213.6
	1.6	212.0	194.1	200.0	384.1	345.3	353.2

TABLE 12: RANGE OF IMPINGEMENT HAZARD

	POOL DIA. 20 m		POOL DIA. 40 m	
WIND V(m/s)	2	4	2	4
Ethanol	3.5	8.3	3.4	9.7
Gasoline	5.9	15.7	5.9	17.4
Hexane	6.7	17.8	6.6	19.4
Toluene	7.8	20.4	7.7	22.3

TABLE 13: UNCONFINED POOL FIRE PARAMETERS
Catastrophic Failure (40,000 kg released)
Raj Correlation
Quiescent Atmosphere

FUEL	VOLUME SPILLED(m^3)	MAX POOL DIA (m)	AVG POOL DIA (m)	AVG FLAME LENGTH(m)	BURNING DURATION(s)
Ethanol	50.4	175.5	112.0	38.4	233.5
Gasoline	54.0	127.9	81.6	68.0	119.8
Kerosene	48.8	137.7	87.8	58.0	146.0
Hexane	61.5	120.7	77.0	78.3	100.0
Toluene	46.1	110.7	70.6	83.5	97.1

TABLE 14: TIME AVERAGED POOL DIAMETER
UNCONFINED POOL FIRE
Catastrophic Failure
Damage to Buildings
SRD τ option

FUEL	SPONTANEOUS IGNITION(kJ/m²)	HAZARD DISTANCE(m)	PILOT IGNITION(kJ/m²)	HAZARD DISTANCE(m)
Ethanol	5951.9	135.5	3179.0	176.4
Gasoline	3061.3	122.4	1645.5	170.5
Kerosene	3726.8	129.5	1998.9	175.5
Hexane	2557.3	85.5	1377.6	132.8
Toluene	2482.7	115.9	1337.9	168.2

TABLE 15: TIME AVERAGED POOL DIAMETER
UNCONFINED POOL FIRE
Catastrophic Failure
Damage Criteria: Integrated Total Dose
SRD τ option

FUEL	375 (kJ/m²)	250 (kJ/m²)	125 (kJ/m²)	65 (kJ/m²)
Ethanol	448.0	537.4	734.7	987.3
Gasoline	343.7	414.7	574.0	770.7
Kerosene	379.7	457.0	627.5	845.8
Hexane	260.9	316.6	438.4	593.8
Toluene	319.2	385.5	535.5	725.3

TABLE 16: DAMAGE CRITERIA: PROBIT DOSE (Hymes)

FUEL	1% LETHALITY	50% LETHALITY	BLISTERING OF SKIN	2ND DEGREE BURNS	3RD DEGREE BURNS
Ethanol	333.9	258.9	574.4	320.5	248.8
Gasoline	272.9	207.2	479.5	261.3	198.2
Kerosene	296.8	226.7	516.0	283.7	217.2
Hexane	209.4	154.9	375.1	199.8	147.2
Toluene	257.7	192.2	459.9	246.2	183.1

TABLE 17: TIME-DEPENDENT UNCONFINED POOL FIRE

Catastrophic Failure (40,000 kg spilled)
Damage Criteria: Integrated Total Dose
SRD τ option: 50% R.H.; 294K; 10 km visual range

FUEL	375 (kJ/m^2)	250 (kJ/m^2)	125 (kJ/m^3)	65 (kJ/m^2)
Ethanol	470.4	563.3	768.4	1030.9
Gasoline	359.4	433.5	596.0	804.0
Kerosene	397.6	478.3	655.6	882.8
Hexane	272.0	330.3	457.6	619.7
Toluene	332.5	403.5	558.6	756.0

TABLE 18: DAMAGE CRITERIA: PROBIT DOSE

FUEL	1% LETHALITY	50% LETHALITY	BLISTERING OF SKIN	2ND DEGREE BURNS	3RD DEGREE BURNS
Ethanol	360.6	280.7	616.7	346.4	270.0
Gasoline	292.7	221.9	513.6	280.1	212.9
Kerosene	318.2	243.9	553.0	305.0	233.8
Hexane	223.1	163.6	401.2	212.8	155.1
Toluene	274.8	203.9	491.7	262.3	194.0

TABLE 19: TRANSIENT FIREBALL PARAMETERS

	17 tonnes		22 tonnes		27 tonnes	
	BUTANE	PROPANE	BUTANE	PROPANE	BUTANE	PROPANE
Mass in Cloud (kg)	4363.4	10600.4	5646.7	13718.1	6930.0	16835.9
Initial Dia. (m)	15.13	22.3	16.5	24.3	17.6	26.0
Final Dia. (m)	93.14	126.4	98.22	137.7	107.5	147.4
Burning Time (sec)	7.2	9.7	7.6	10.6	8.4	11.3
Final Elevation (m)	72.0	97.3	76.4	106.0	84.0	113.0

TABLE 20: TRANSIENT FIREBALL
Catastrophic Failure
SRD τ: 50% R.H., 10 km visibility, 294K
Total Dose (kJ/m²)

	17 tonnes		22 tonnes		27 tonnes	
Q (kJ/m²)	BUTANE	PROPANE	BUTANE	PROPANE	BUTANE	PROPANE
375	-	115.5	-	137.2	51.2	154.0
250	75.3	170.0	106.9	196.7	104.5	217.7
125	145.3	272.5	197.8	310.6	186.7	341.0
65	220.6	393.1	299.3	445.6	278.2	487.6

TABLE 21: DAMAGE CRITERIA: PROBIT DOSE

	17 tonnes		22 tonnes		27 tonnes	
PROBIT DOSE	BUTANE	PROPANE	BUTANE	PROPANE	BUTANE	PROPANE
1060	54.25	137.3	64.4	158.1	77.8	176.5
2300	-	44.1	-	61.2	-	75.4
2600	-	-	-	39.1	-	54.5
1200	41.3	124.2	51.8	143.9	64.7	161.3
210	187.8	326.5	205.7	366.8	233.0	402.0

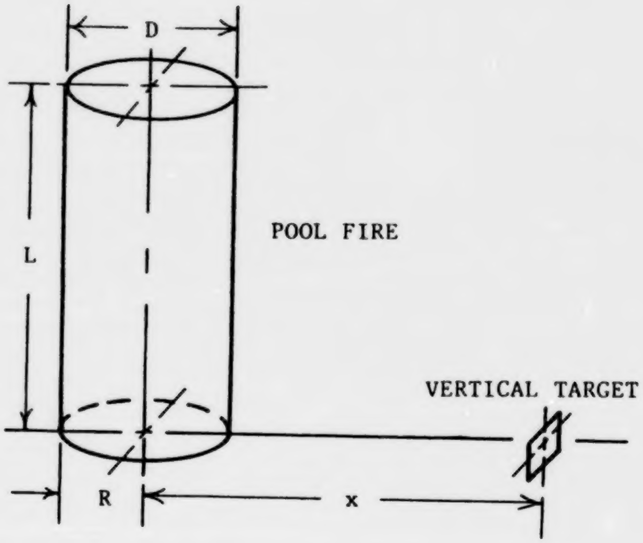

D
L
POOL FIRE
VERTICAL TARGET
R
x

Figure 1:
Cylindrical Solid Flame Pool Fire Model

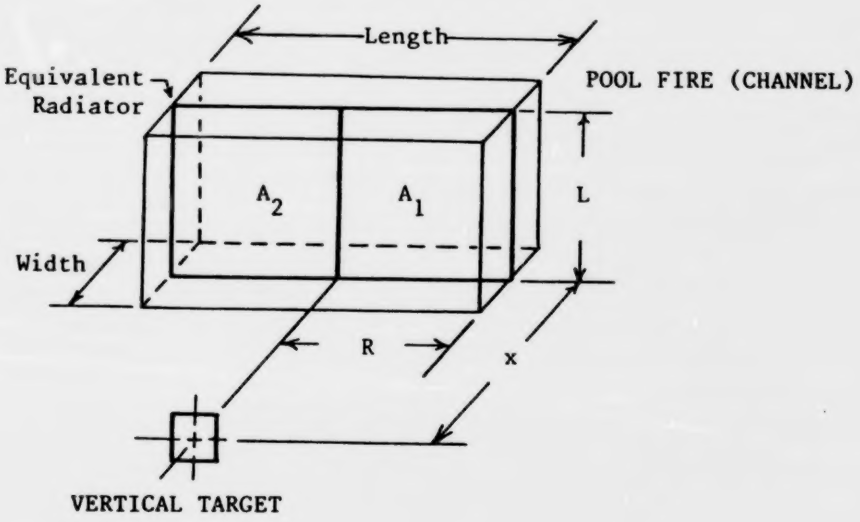

Length
Equivalent Radiator
POOL FIRE (CHANNEL)
A_2
A_1
L
Width
R
x
VERTICAL TARGET

Figure 2:
Rectangular Pool Fire Equivalent Radiator Model

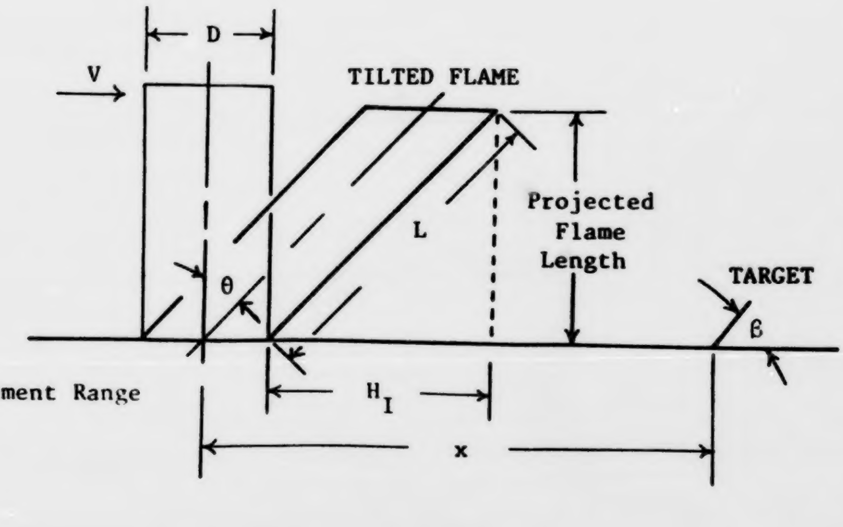

D
V
TILTED FLAME
L
Projected Flame Length
θ
TARGET
β
H_I
x

Figure 3:
Tilted Flame Pool Fire Model

H_I = Impingement Range

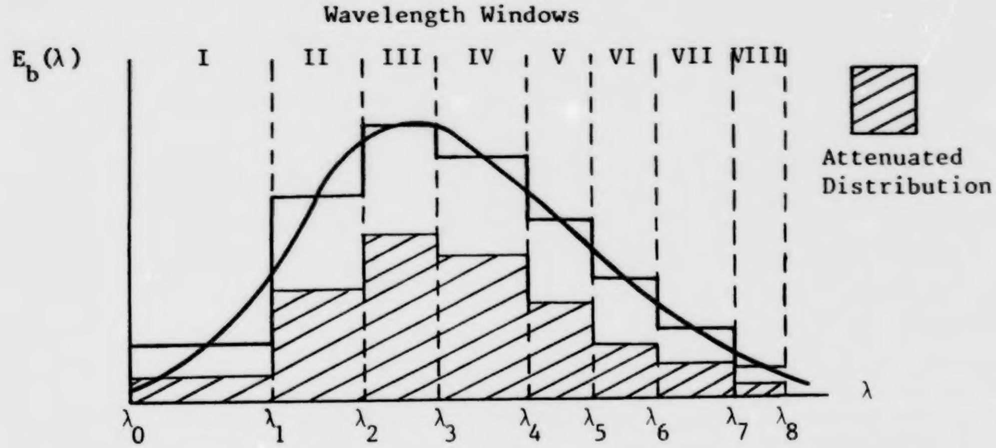


Figure 4: Blackbody Spectrum for Flame

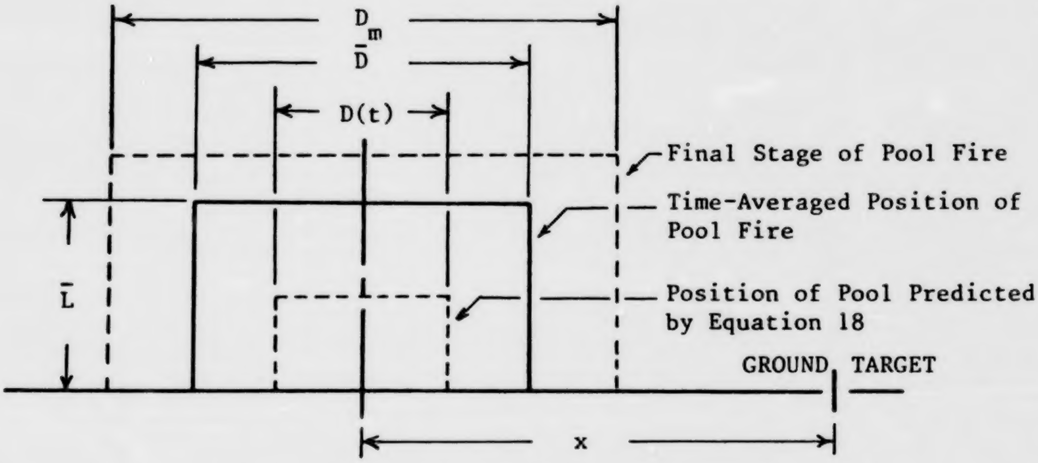

D_m
$\bar{D}$
D(t)
Final Stage of Pool Fire
Time-Averaged Position of Pool Fire
$\bar{L}$
Position of Pool Predicted by Equation 18
GROUND
TARGET
x

Figure 5: Mudan Unconfined Fire Model

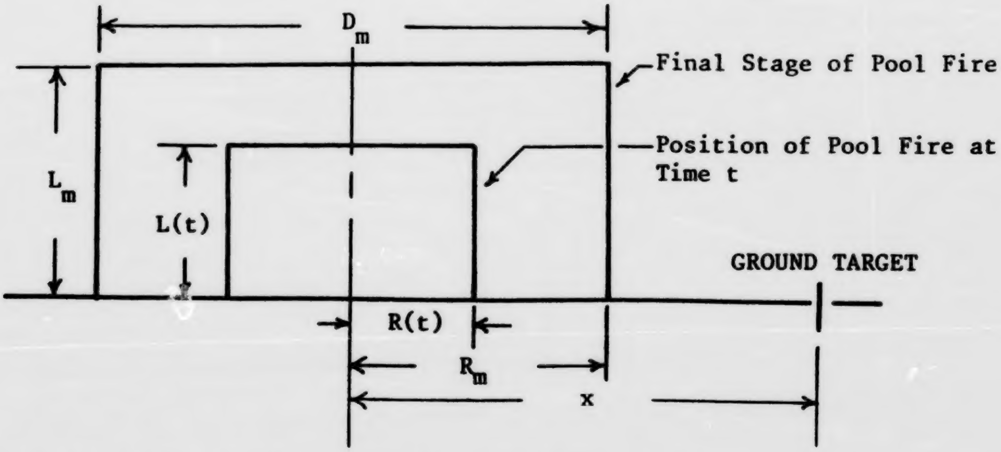

D_m
Final Stage of Pool Fire
Position of Pool Fire at Time t
L_m
L(t)
GROUND TARGET
R(t)
R_m
x

Figure 6: Time-Dependent Unconfined Pool Fire Model

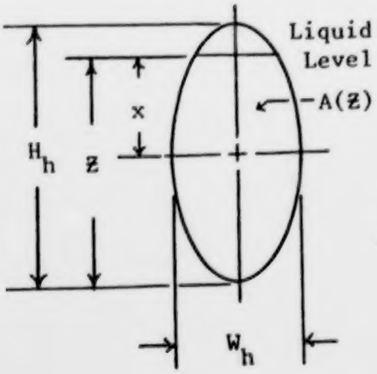

Liquid
Level
A(Z)
x
H_h
Z
W_h

Figure 7a: Effective Rupture Area of Hole

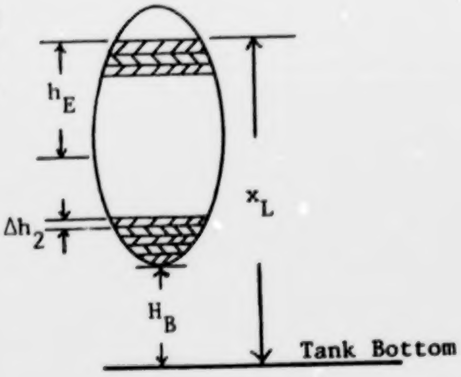

h_E
Δh_2
x_L
H_B
Tank Bottom

Figure 7b: Level Decrement Geometry in Discharge Model

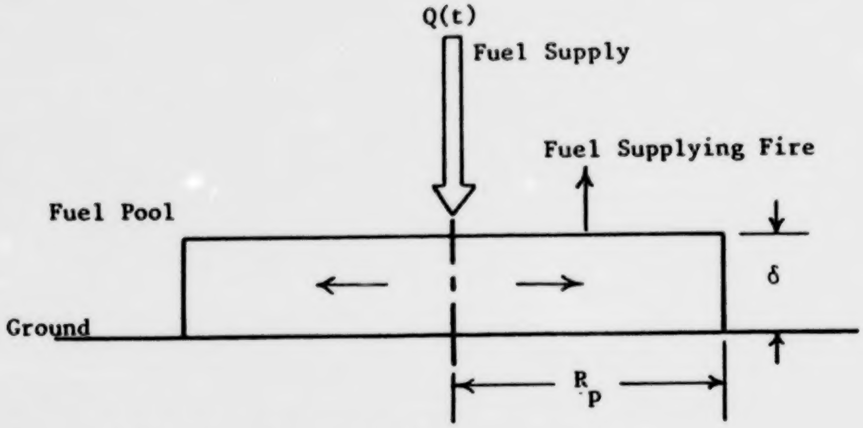

Q(t)
Fuel Supply
Fuel Supplying Fire
Fuel Pool
Ground
δ
R_p

Figure 8: Spill Fire Growth Model

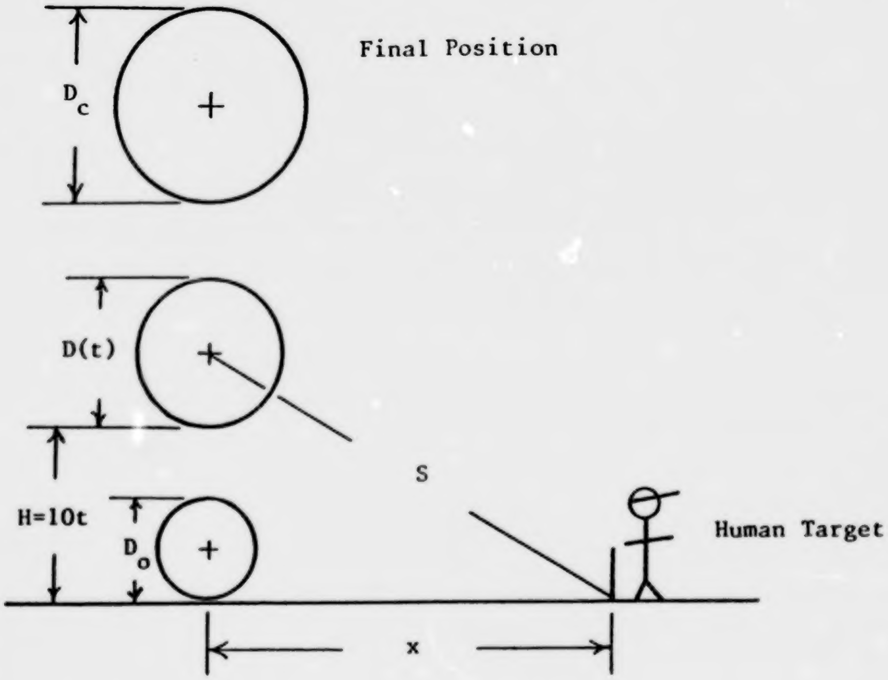

Final Position
D_c
$D(t)$
S
H=10t
D_o
Human Target
x

Figure 9: Isothermal Time-Dependent Fireball Model

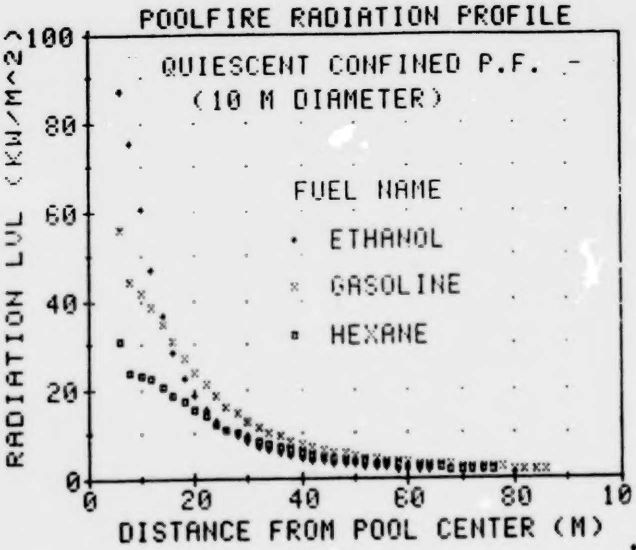


Figure 10

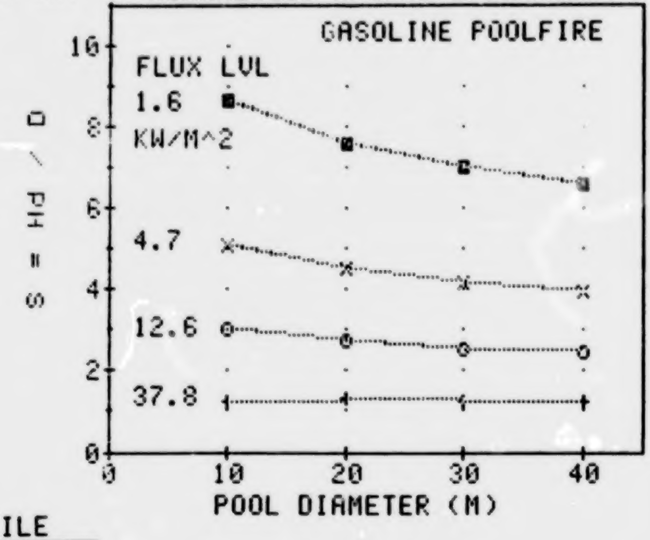


Figure 11

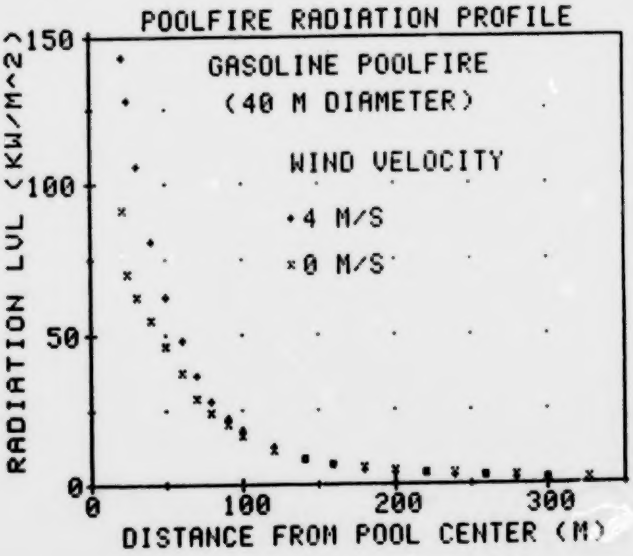


Figure 12

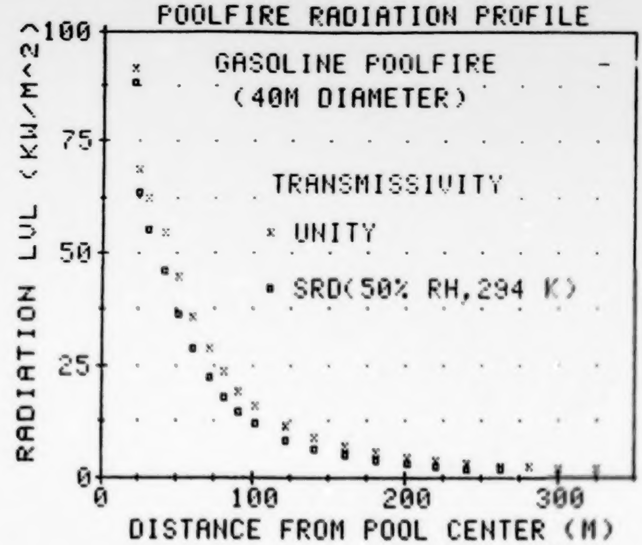
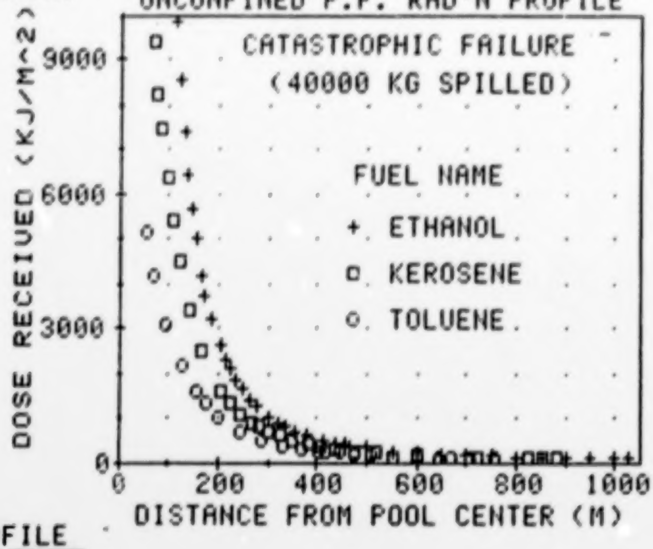


Figure 13

Figure 14



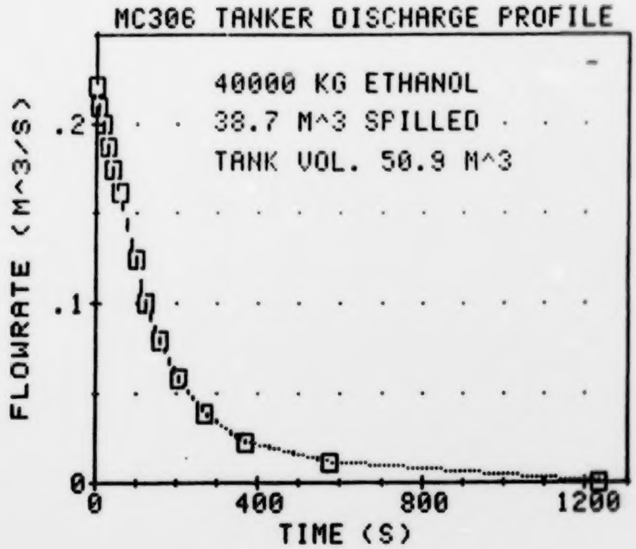


Figure 15

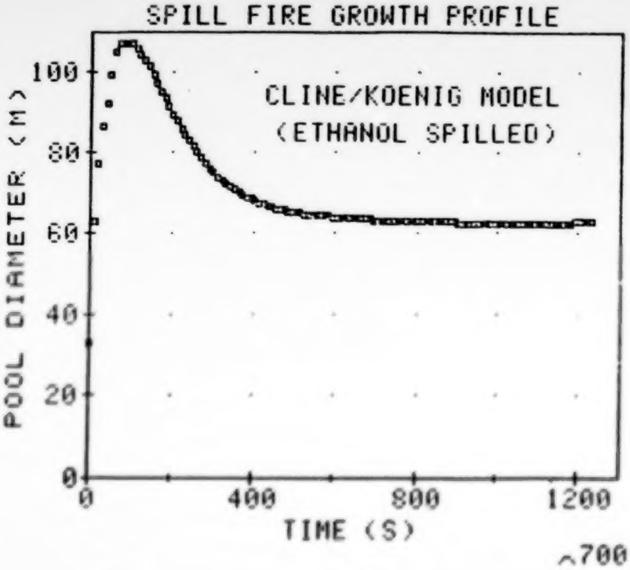


Figure 16

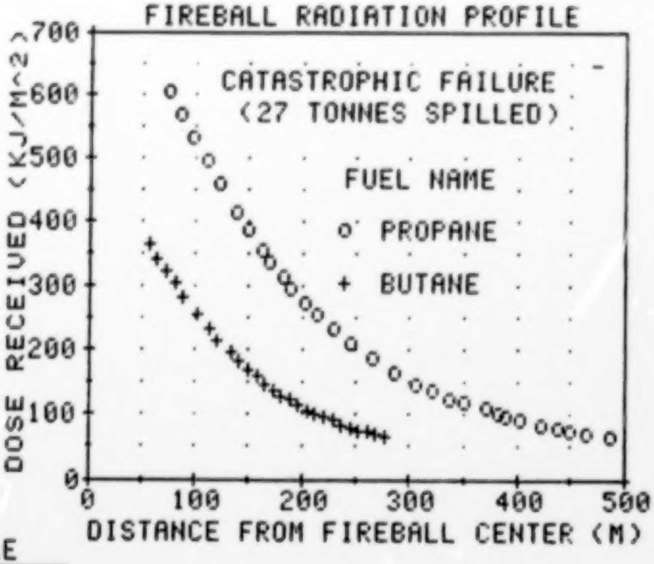


Figure 17

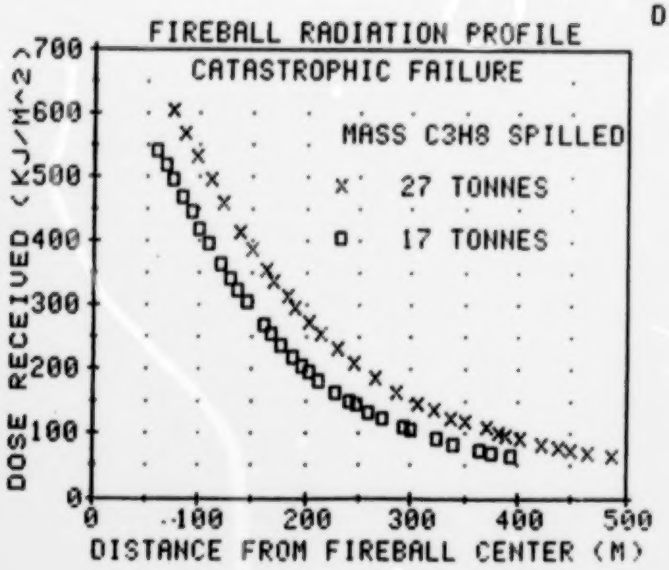


Figure 18

COMPARISON OF A HEAVY GAS RELEASE MODEL WITH FIELD DATA

H. Sahota, P.K. Misra

Ministry of the Environment
Air Quality and Meteorology
Air Resources Branch
125 Resources Road, East Wing
Rexdale, Ontario
M9W 5L1

ABSTRACT

A simple box model for heavy gas dispersion is modified to include the effects of wind shear in the surface layer. Instead of the usual assumption that the heavy gas cloud moves instantaneously, initial acceleration of the cloud is also accounted for. The model is verified with data from Thorney Island Field Trials. The results indicate that the location of the cloud is predicted with more accuracy when the effects of wind shear and initial acceleration are accounted for.

1. INTRODUCTION

During the past two decades, there has been a very rapid increase in the use of toxic chemicals in the manufacturing industries. The most common mode of transportation of these chemicals is either by rail or tanker trucks. In either case, in the event of a spill they pose series threat to the environment. There have been quite a number of accidents in which large amounts of toxic chemicals were released into the environment causing substantial damage and some cases of death.

The literature is abundant on the dispersion processes related to buoyant gaseous clouds. However, only recently, the problem of dispersion of denser than air gases has been addressed. Blackmore et al.(1) compiled a comprehensive list of currently available mathematical models. These models can be classified into three groups: (1) Box Models, (2) Similarity Models, and (3) Numerical Models Based on Navier Stokes Equations. Models in category 2 and 3 are generally more complex than the box models and require substantial computer resources and thus are not suitable for emergency response situations. In comparison the box models are comparatively simple to use and can be implemented on a small personal computer.

The box models treat the dispersion of the gaseous cloud in two phases. In the first phase, the cloud is assumed to slump in a self similar manner i.e. the shape of the cloud is preserved. The duration of the slumping phase is a function of the initial height of the cloud and the density difference of ambient air and the cloud. Slumping phase is assumed to terminate when atmospheric turbulence rather than gravity dominates the dispersion process. During the second phase, ambient air is entrained into the cloud and both radius and height of the cloud increase with time.

In addition to determining the size of the cloud and concentrations within, horizontal advection of the cloud by the surface winds is required in the event of an accidental spill. In most of the box models, the advecting wind is assumed to be constant and some function of 10 m winds. For example Eidsvick(2) defines the advecting wind as:

$$U^2 = \left(\frac{2}{3} U_f\right)^2 + U_a^2 \qquad (1)$$

where: 'U' is the representative free stream velocity of the cloud, 'U_f' is the average gravity flow and 'U_a' is atmospheric wind speed usually at 10 m. Equation 1 implies that 'U' > 'U_a' as 'U_f' > 0.

It is known that the gaseous cloud slumps rapidly with time. In view of the strong gradients in wind speed which exist near the surface we expect the transport wind to be a function of downwind distance and different from the 10 m wind. This paper describes a method to include the effect of wind shear on the transport wind into the box models in a realistic manner. It is shown that better correlation with experimental data is obtained by this method.

2. DISPERSION OF THE CLOUD

Like most other box models of heavy gas dispersion [Weber (3)], we use the gravity intrusion expression (Equation 1) during the slumping phase.

$$dR/dT = \frac{C\left[\rho_g - \rho_a\ g\ h\right]^{1/2}}{a} \qquad (2)$$

where: C: Froude No.

R: Radius of the cloud

o_g: Density of the gas
o_a: Density of ambient air
h: Height of the cloud
and g: Universal acceleration constant

Van Ulden(4) suggests a value of 1 for 'C', which is supported by Thorney Island data which indicates a mean value of 1.05.

Treatment of Horizontal Advection

The determination of horizontal displacement of the cloud is important because it gives the exposure time and the dosage received by the target. The rate of collapse of the heavy gas cloud is inversely proportional to the density differential between the gaseous cloud and the ambient air. Figure 1 shows the rate of collapse for a mixture of Nitrogen and Freon gas. It takes only a few seconds for the cloud to reach 1/10 th of its initial height. It is known that the winds in the surface layer possess a nearly logrithmic profile under neutral and slightly stable conditions. Consequently, as the cloud slumps, it is exposed to winds which are decreasing in magnitude. The procedure we have followed to account for this wind shear is as follows:

We use equation 3 for specifying the wind profile in the surface layer as suggested by Van Ulden(5):

$$u = u_*/k \left[\ln(z/z_o) - \Psi(Z/L)\right] \qquad (3)$$

where: u_*: Friction velocity
k : Von Karman's constant taken as .4
z_o: Surface roughness
and $\Psi(Z/L)$: $= -4.7\ Z/L$ for stable conditions
$= 0$ for neutral
$= 2 \log[1+a)/2] + \log (1+a)/2-$

$\tan^{-1}(a) + \Pi/2$ for unstable

'a' is defined as $a = (1-15\ Z/L)$ and 'L' is the Monin-Obukhov length.

Equation 2 is integrated with respect to time and height to obtain the average wind acting on the cloud as a function of time. We denote this average wind as the transport speed of the cloud.

The cloud height 'h' for substituting in Equation 3 is simply obtained by assuming that the shape of the cloud is conserved and that no entrainment occurs during the slumping phase.

$$h = V/A$$

where h: Height of the cloud
V: Volume of the cloud
and A: Area of the cloud

Equation 4 gives the cloud area for any time 't':

$$R = [\ R_o^2 + 2\beta t]^{1/2} \qquad (4)$$

where R_o = Radius at time 't_o'

and $\beta = - \dfrac{[(\rho_g - \rho_a\ )\ g\ V]^{1/4}}{\rho_a}$

Inclusion of the Acceleration Period of the Cloud

The data of Thorney Island experiments show the entrainment of ambient air into the cloud during slumping phase to be small. Since the constant 'C' in Equation 2 did not change from unity significantly, neglecting entrainment effects the acceleration of the cloud can be simply defined as:

$$dV/dT = \frac{1}{M} \cdot \left[D-f\right] \qquad (6)$$

where V = Velocity of the cloud

M_g = Mass of the cloud

D = Drag force acting on the cloud

F = Frictional force acting on the cloud

Following Noel de Nevers(6) we define the drag and frictional forces as:

$$D = R H \sigma_a u^2 C_d \qquad (7)$$

$$F = \pi R^2_o \sigma_g (u^2/2) f \qquad (8)$$

where u: Free stream velocity

C_d: Drag coefficient, taken here as unity

and f: friction factor which is given by [Gifford(7)]:

$f = 2 \left[u_*/u\right]^2$

The cloud accelerates and attains its terminal velocity when the drag force is balanced by frictional force. The acceleration period will last until:

$$R/H = \frac{2\sigma_a}{\pi \sigma_g f} \qquad (9)$$

For Thorney Island trials R/H was about 74, which occurred around the 10 second mark from the start of the spill. This compares well with the observed acceleration periods which typically lasted from 5 to 10 seconds. Rottman and Hunt(8) used a vortex in all methods to study the instantaneous release of a puff. For low Reynolds number they observed that the acceleration period could be defined by $t_a = cr_o/U_o$, where r_o and U_o are the initial radius and wind speed and e is a constant. Typically the acceleration period was between 2 to 7 seconds. If we assume constant acceleration of the cloud, the cloud velocity can be defined as:

$$U_{cloud} \doteq U_E \left[(R_E/H_E)/(R/H)\right] \qquad (10)$$

where 'R_t' and 'H_e' are the cloud radius and height at any time 't' and R and H are the radius and height when the slumping phase terminates.

3. MODEL EVALUATION

Safety and reliability Directorates of United Kingdom Atomic Energy Authority conducted a set of experiments at Thorney Island [McQuaid (9)] between the summer of 1982 and summer of 1984. A mixture of Freon12 and Nitrogen was used to simulate a heavy gas. Overhead photographs along with relevant meteorological data were collected for all the trails. Out of fifteen trials conducted under light to moderate winds, data from six trials, trial Nos: 7,8,9,11,13 and 14 were selected for model verification. Trial No. 7 to 11 were low wind trials (wind <3.5 m/s) and trial No. 13 and 14 were conducted under moderate winds (winds around 7 m/s).

Trial No. 7 (Sept. 8, 1982: Time of Release: 19:33:20):

Under cloudy skies, winds were from south-southeast at about 5 m/s. Due to overcast conditions the solar insolation was slight to moderate at 350 w/m^2 and the atmospheric stability was determined to be 'D'. The model was run with 3.2 m/s mean wind at 10 m level and with 'D' stability. Figure 2 shows the observed and predicted location agree well upto about 20 sec mark. After that time the observed position of the cloud centroid tends to travel at faster speed than that predicted by the model. One possible explanation is that the winds started to pick up again or the cloud outline was not visible completely thus introducing some error in the centroid location.

Trial No. 8 (Sept. 9, 1982; Release Time: 17:49:58):

About four hours prior to the release, under partly cloud skies the winds were at about 5 m/sec. Solar insolation was at 135 w/m^2. These conditions gave Pasquill-Gifford 'D' stability. By the release time the winds dropped to about 2.5 m/sec. The model predicted cloud centroid locations agree well (Figure 3.) with the observed location upto 20 sec. from the release time. After that the model predicts that the cloud is travelling at a speed lower than that observed. At about fifty second mark the error is about 15 meters in the cloud centroid location.

Trial No. 9 (Sept. 15, 1982: Release Time: 18:45:20):

Few hours prior to the release time, the solar insolation was moderate at about 600 w/m^2 with 4.5 m/s winds at ten metres. Atmospheric stability was determined to be Pasquill-Gifford class 'B'. By the release time insolation had decreased gradually along with a drop in the wind speed to about 2 m/s and the stability changed from 'B' to 'D/E'. The model was run with mean wind speed of 1.7 m/s and 'D' stability.
Figure 5 shows the comparison between the observed and the model predicted cloud centroid locations. At the five second mark, there is a discrepancy of five meters between the observed and the model predicted locations. However, after the ten second mark the agreement improves significantly. The initial error could be due to low winds and in the interpretation of the visual records in determining the cloud centroid.

Trial No. 11 (Oct. 10, 1982; Time of Releases: 17:21:46):

About two hours before the release, under cloudy skies, winds were around 5 m/s and the stability was 'D'. By the release time the sky was almost overcast and the stability was judged to be 'E'. There was a slight drop in the wind speed prior to the main data collection period. The wind speed during spill was 5.1 m/sec. Figure 6 shows the comparison between the observed and model predicted locations of the cloud centroid. The model slightly underpredicts the centroid location.

Trial No. 13 (Oct. 19, 1982; Time of Release: 11:41:11):

About two hours prior to the release, the solar insolation was slight giving stable conditions. There was gradual increase in the insolation till the release time. Mean winds prior to the release were around 4 m/s, however during the release they were measured at 7.5 m/S. During the release time the stability was class 'D'. Figure 7 shows the comparison between the observed and predicted cloud centroid locations. The agreement between the observed and predicted location is very good at all times.

Trial No. 14 (Oct. 24, 1982; Release Time: 11:57:49):

Few hours before the release, winds were low (around 1 m/s) and the insolation was slight giving 'D' stability. Winds were steadily increasing and by the release time reached 4.6 m/s. During the data collection period winds were observed to be around 7 m/s. There was slight increase in the insolation, however stability was near neutral to slightly stable. Figure 8 shows the model predicted and observed locations of the cloud centroid. The slope of the predicted location curve matches that of the observed locations upto the 5 sec. mark. Thereafter, the model predicted locations are consistently higher by about 8 meters. This could be due to errors in the wind speed data. The slope of the predicted and observed location curve match well after the 10 second mark.

Effect of the Acceleration Term

The model was run with and without the acceleration term of equation 5 to determine its affect on the cloud location. Figures 9 and 10 show the affect of the acceleration term for trials 7 and 13. If the initital acceleration of the cloud is neglected then the model advects the cloud at a higher speed. By including the initial acceleration of the cloud, the agreement between the observed and predicted cloud locations improves significantly.

Conclusions

We have shown that a simple box model of heavy gas dispersion can predict the cloud centroid location with reasonable accuracy if the initial acceleration of the cloud is accounted for. The model was developed and implemented on a PC for field use. It takes about four to five minutes to complete one simulation of one hour real time.

The model was verified with the data from Thorney Island field trials. Model predicted cloud centroid locations agree well with the observations. The agreement is better for wind speeds greater than 3 m/s (Trial Nos. 7,11,13 and 14).

Acknowledgements

We would like to thank Atmospheric Environment Services (Environment Canada), a co-sponsor of the Thorney Island experiments, for providing the data.

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Figure 4: Same as Figure 2 but for Trial #9.

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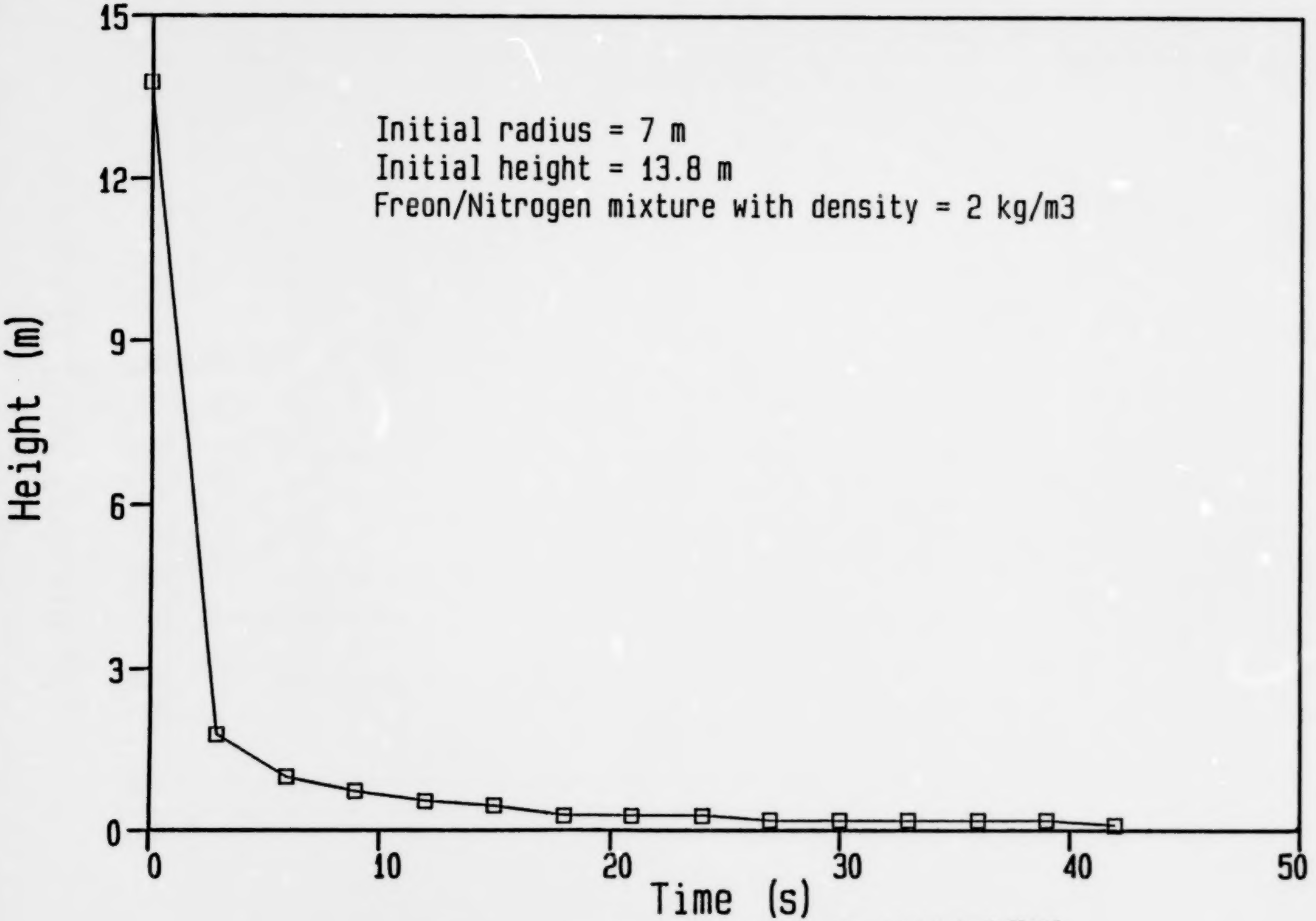
Figure 9: Same as Figure 8 but for Trial #13.



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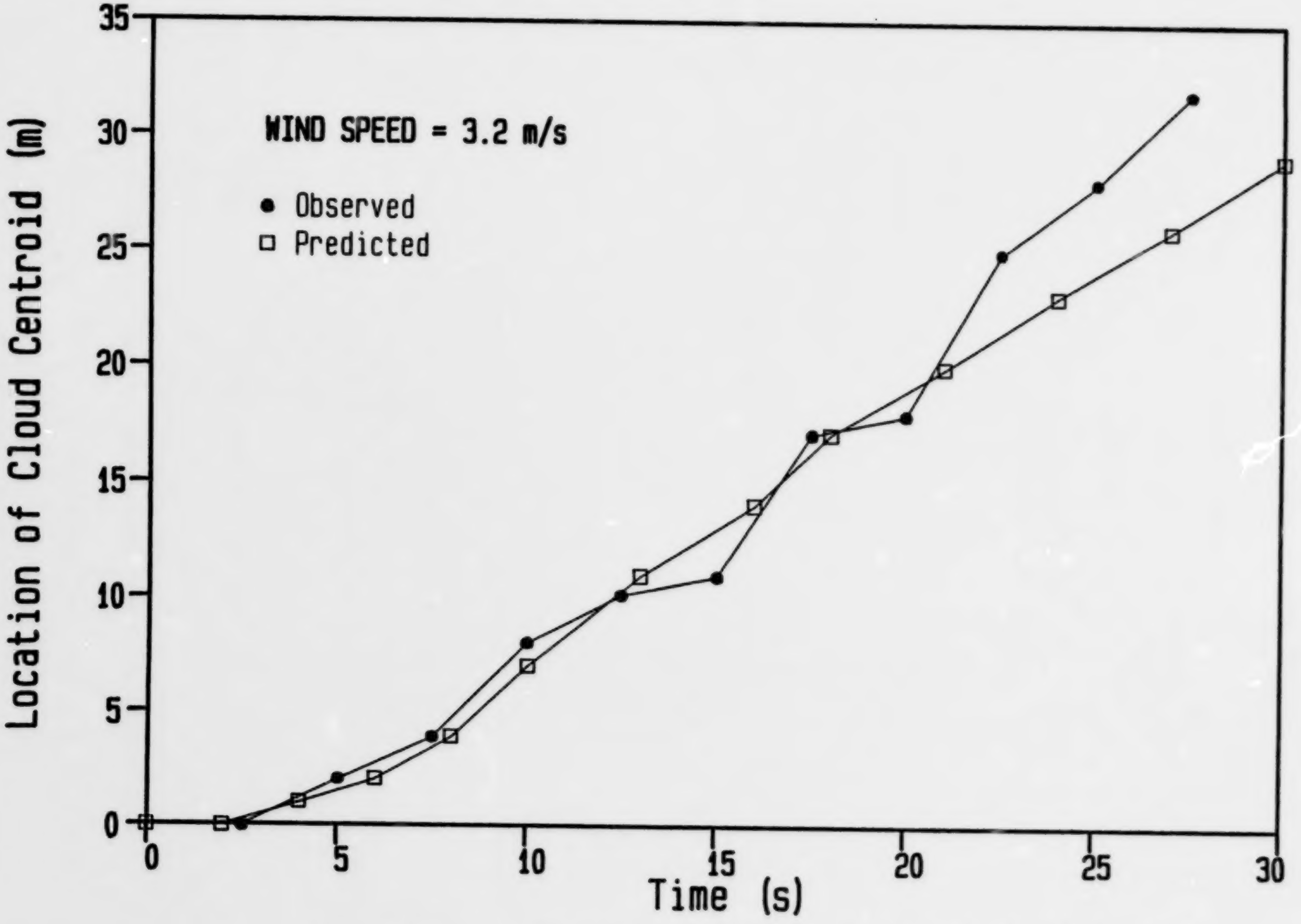
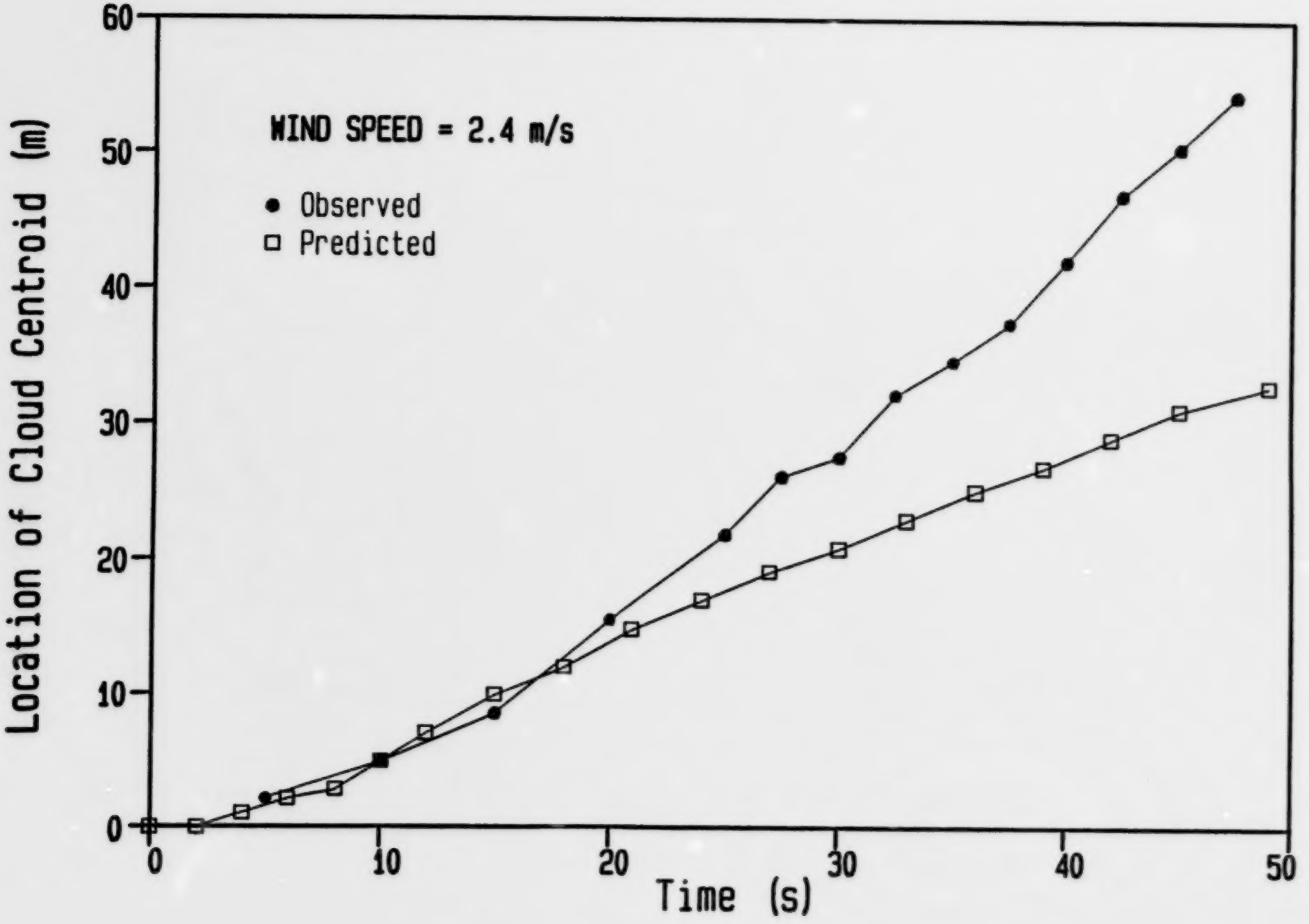


Figure 2: Observed and Model Predicted Cloud Centroid Locations for Trial #7 at Thorney Island.



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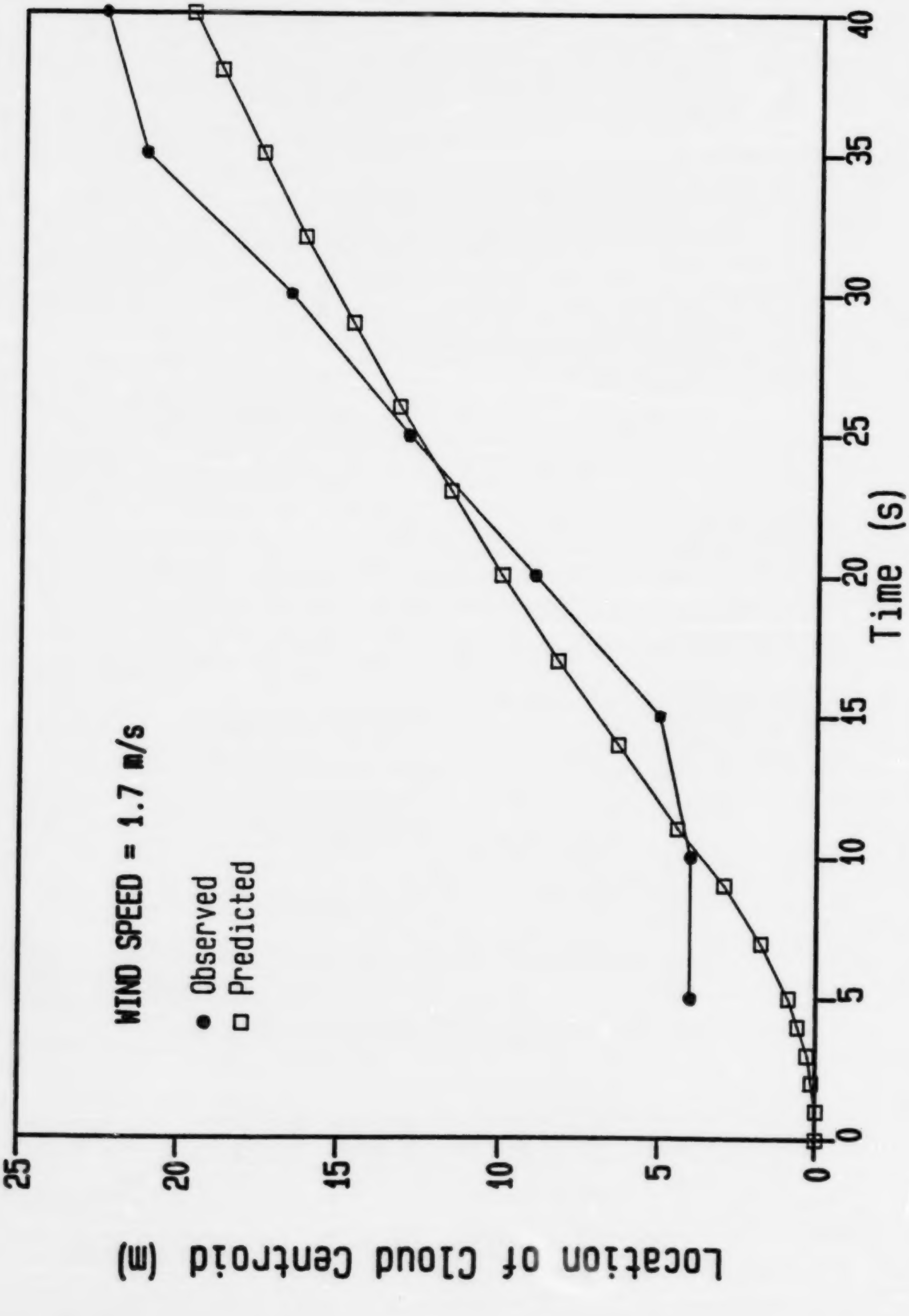

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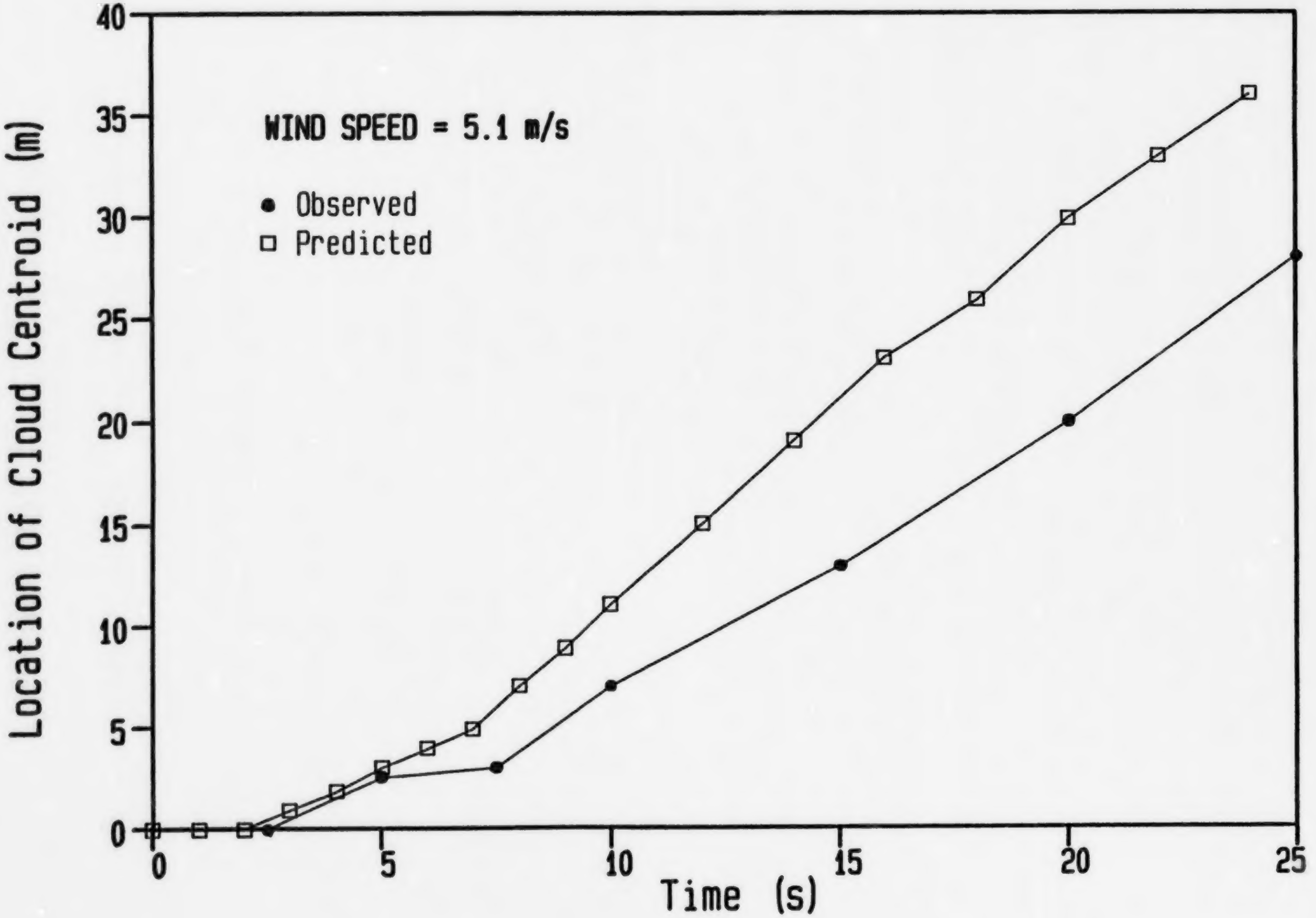

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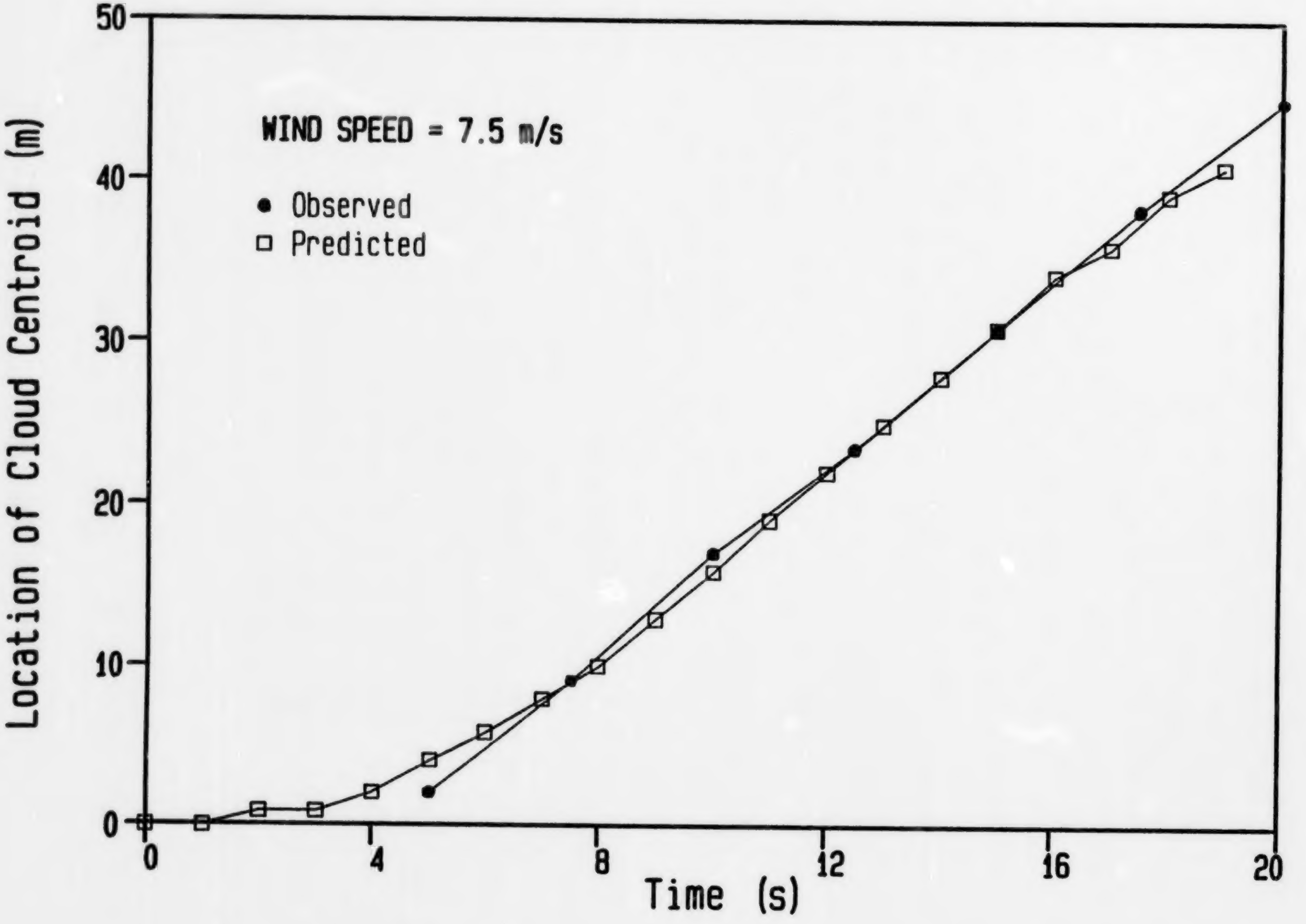

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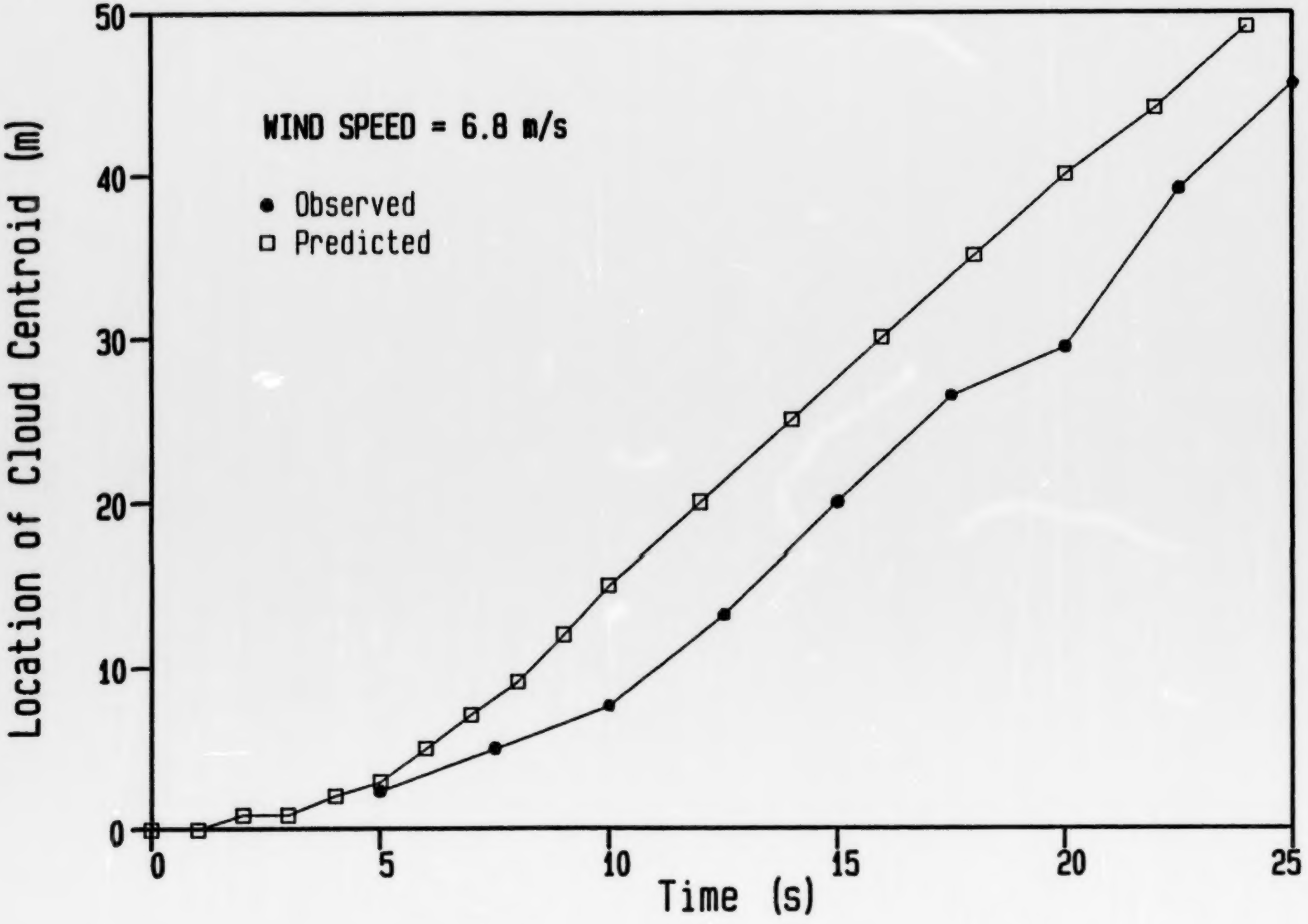

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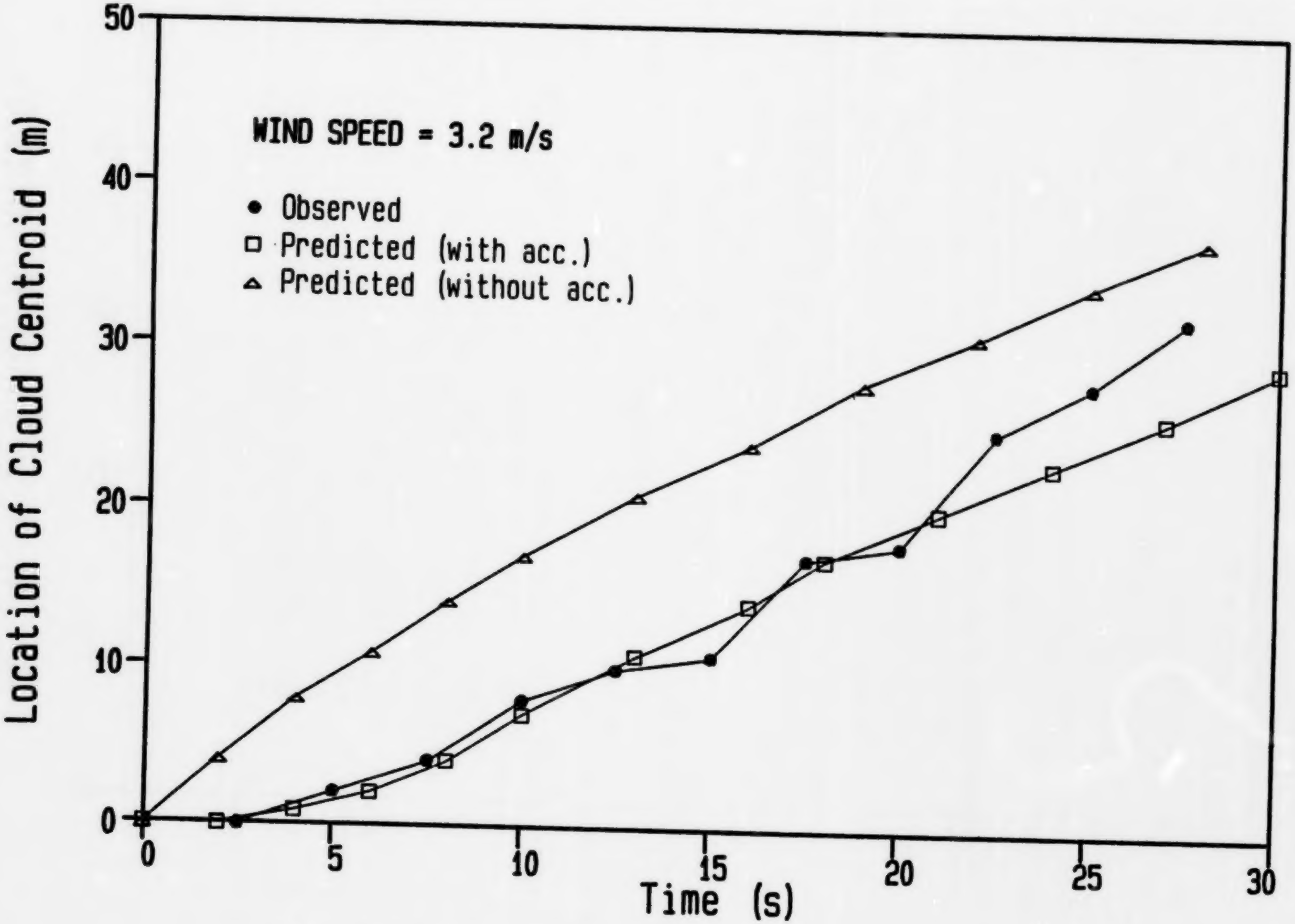

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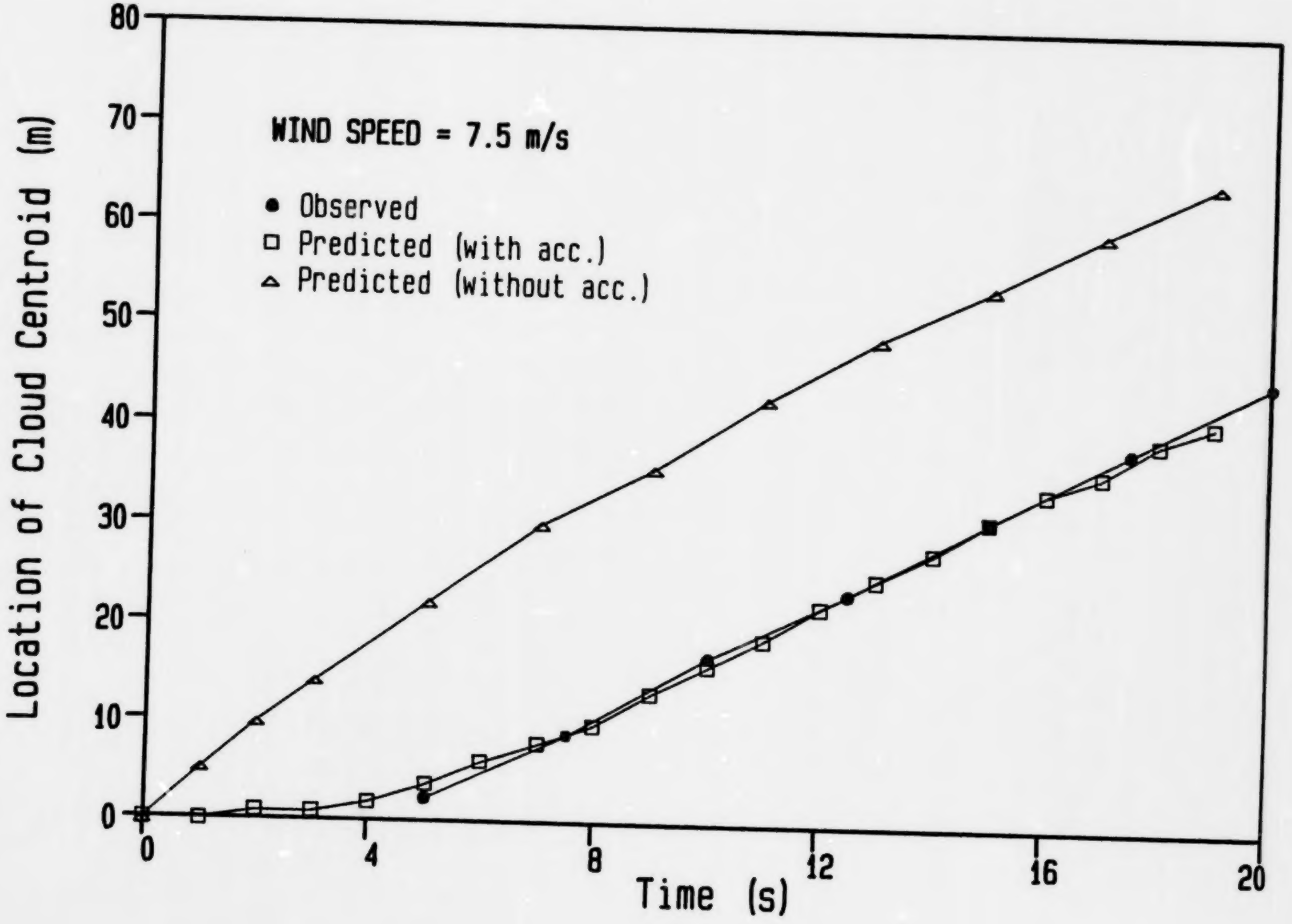


Figure 9: Same as Figure 8 but for Trial #13.

WHAT IS A BLEVE?

CA McDevitt, FR Steward, JES Venart
University of New Brunswick

ABSTRACT

Loss of containment of liquified gases or of pressurized liquids at a temperature above their normal boiling point can result in a BLEVE - a Boiling Liquid Expanding Vapour Explosion. Classic and recent examples of this phenomenon are reviewed.

The main theories on the causes of a BLEVE are discussed in light of recent incidents. Comments are made on current literature discussion about the definition of a BLEVE.

Research about the mechanism of BLEVEs is being conducted at the University of New Brunswick. Of particular concern is whether the flammability of the tank contents is a factor. The possibility that BLEVEs may be prevented by keeping the container below the pressure associated with the superheat temperature limit is also of interest. This research is discussed and experimental results are given.

INTRODUCTION

A BLEVE is a Boiling Liquid Expanding Vapour Explosion. It is defined as a major container failure, into two or more pieces, at a moment in time when the contained liquid is at a temperature well above its boiling point at normal atmospheric pressure, T_{nb}.(1) The term BLEVE was first coined in 1957 by Factory Mutual to simplify discussion of explosions which have flash evaporation as their energy source.(2) The BLEVE sequence of events is as follows:

1) Loss of containment of a liquid which is above T_{nb}. The container may be fractured due to impact, fire impingement, corrosion or overpressure. Liquified gases are carried above T_{nb} and may be subject to BLEVEs. Under fire exposure it is possible that any liquid may also fit in this category.

2) Rapid boiling of the fluid as the pressure is reduced to atmospheric. This rapid boiling is the physical explosion which blows the container apart.

3) The rapid boiling has now produced a vapour cloud. If the vapour cloud is flammable, a fireball may ensue. It is important to note that at the time of the fireball, the explosion has already occurred. The overpressure associated with the blast and the blowing apart of the tank car are not related to the fireball.

EXPLOSIVE EXAMPLES

Crescent City, Illinois, 1970

A train derailment in the business section of Crescent City caused a fire. The train was carrying propane tank cars, which were engulfed in the fire. The local fire department evacuated the area and then attempted to cool the cars by applying water to the vapour space. After some time, the pressure relief valves on some of the tank cars began to operate. Sixty-three minutes after the fire began, one tank car exploded. A few minutes later, two more tank cars BLEVEd.(3)

Kingman, Arizona, 1973

Two operators were unloading an LPG (liquified petroleum gas) tank car when a fire started from a leak at a coupling. The fire resulted in a torch flame impinging on the vapour space at the top centre of the car. Some minutes later the PSV (pressure safety valve), which was set at 20.3 bar, began to lift. These vapours also caught on fire. The fire fighters were not able to cool the top of the tank because of necessarily awkward positioning. There was also no near source of water. Between 15 and 40 minutes after the fire began, the tank car exploded and a large fireball resulted. 13 people were killed and 95 were injured. Large tank parts were propelled 365 metres.(4) (See figure 1)

The loss of containment at Kingman was due to the impingement of the flame on the vapour space of the vessel. If a fire contacts a tank in the liquid region, heat added by the fire is removed by the vaporization of the fluid near the wall. The metal temperature cannot then go much above the boiling temperature of the fluid at the contained pressure. However, in the vapour space there is no liquid to boil and remove heat with its heat of vaporization. The metal can be weakened and fail due to the high temperatures.

Once containment was breached, the pressure inside the tank reduced to atmospheric. This allowed vaporization of the propane. The vapour cloud was ignited, probably by the fire, and a fireball resulted. (See Figure 1)

Los Alfaques, Spain, 1978

A tank truck loaded with propylene exploded beside a campsite, killing 210 people. The truck was overloaded, had no relief device and had previously been used to carry anhydrous ammonia which has a weakening affect on steel. The exact course of events is still uncertain. It is known that there was an initial release of propylene which caught fire and burned at the tank truck. A short time later, the vessel exploded. (See figure 2)

The loss of containment could have occurred because of the increase in internal pressure due to the heating of the contents by the fire. The metal was weakened from the carriage of ammonia, and by the flames. There was also the possibility that the vessel had hit a wall, which would have further weakened it and may have been the cause of the first fire. With no pressure relief device, the vessel split open and exploded.(5) (See Figure 2)

San Juanico, Mexico, 1984

A series of explosions occurred at an LPG distribution facility near Mexico City which claimed the lives of about 550 people and injured 7000. Initially there was a large leakage of gas from an unknown source inside the complex. A vapour cloud resulted. This cloud was ignited from an open flame inside the complex and a vapour cloud explosion occurred. This started many ground fires. 1 minute 9 seconds after the vapour cloud explosion, a very heavy explosion was registered - the explosion of one or two of the six LPG spheres. The fires in the complex and flying tank fragments caused a total of 8 container explosions, ranging in time from the first one at 1 minute 9 seconds to 1 hour 17 minutes after the initial vapour cloud explosion. (See figure 3)

It was concluded by the investigators that the first vessel to explode may have been overfilled. Relief valves on the spheres were set at 11.3 bar.(6) (See Figure 3)

Chernobyl, USSR, 1986

An attempt was made to run a nuclear reactor at a known unstable condition. The reaction took off, heating the contents of the reactor above the fuel melting point. As the fuel melted, it fragmented into the cooling water. With the large surface area available for heat transfer, the liquid cooling water vaporized. The volume expansion caused a dramatic pressure rise which blew a hole in the top of the reactor. This is a basic steam explosion.

In this case, the explosion was not caused by a loss of containment, but loss of containment was caused by the explosion. The heat source for the vaporization of the fluid was the nuclear fuel. No outside event caused the vessel to break open before the internal pressure exceeded the vessel strength. However, the explosion was due to a boiling liquid, the cooling water.(7)

In summary,

TABLE 1

	CRESCENT CITY	KINGMAN	LOS ALFAQUES	SAN JUANICO	CHERNOBYL
DEATHS (INJ)	-	13 (95)	210	550 (7000)	31 (300)
NUMBER, TYPE, CONTAINED VOL INVOLVED	3 tank cars	1 tank car (128 m^3)	1 tank truck (38 m^3)	2x2400 m^3 4x1600 m^3 48 hor cyl	-
MATERIAL	LPG	LPG	propylene	LPG	water
PSV SET(bar)	?	20.3	-	11.3	0.8

THEORIES

A pressurized container is a necessary condition for a BLEVE. Conditions inside the vessel must be such that when containment is breached a rapid boiling will take place. The fluid boils with such ferocity that a shock wave is formed, and the tank is torn. Containment is NOT necessary for a boiling liquid expanding vapour explosion. There are many examples of what are termed physical or vapour explosions in liquid-liquid systems.(8,9) This type of explosion is of main concern in the metallurgical and paper industries, as well as the nuclear power generation field. These liquid-liquid boiling explosions occur in systems where the liquids are immiscible, and one is at a

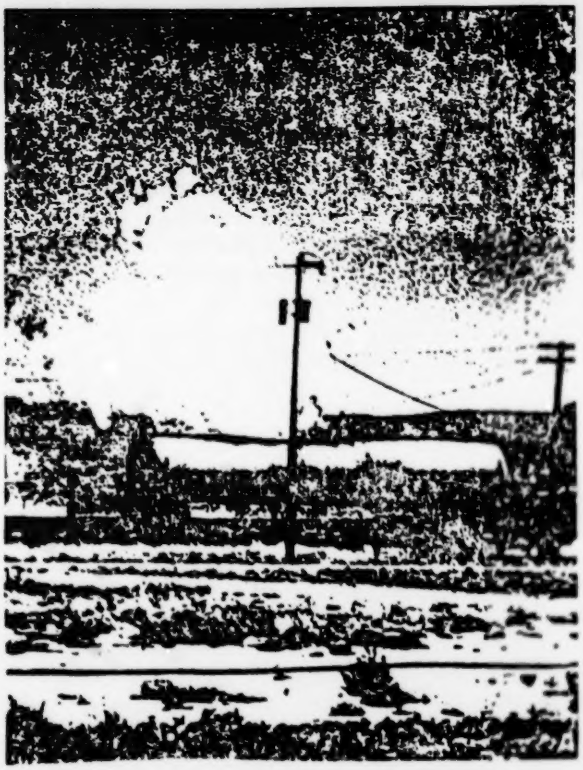


Fig 1 Kingman (4)

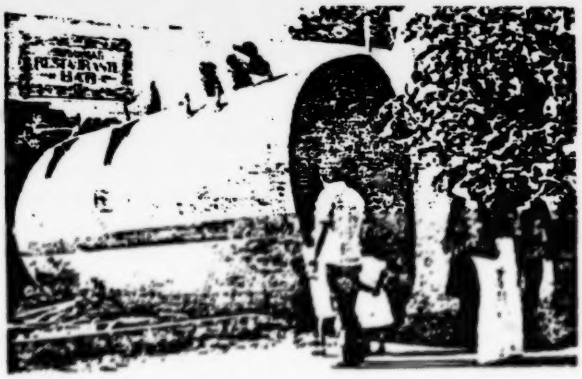


Fig 2 Los Alfaques (5)

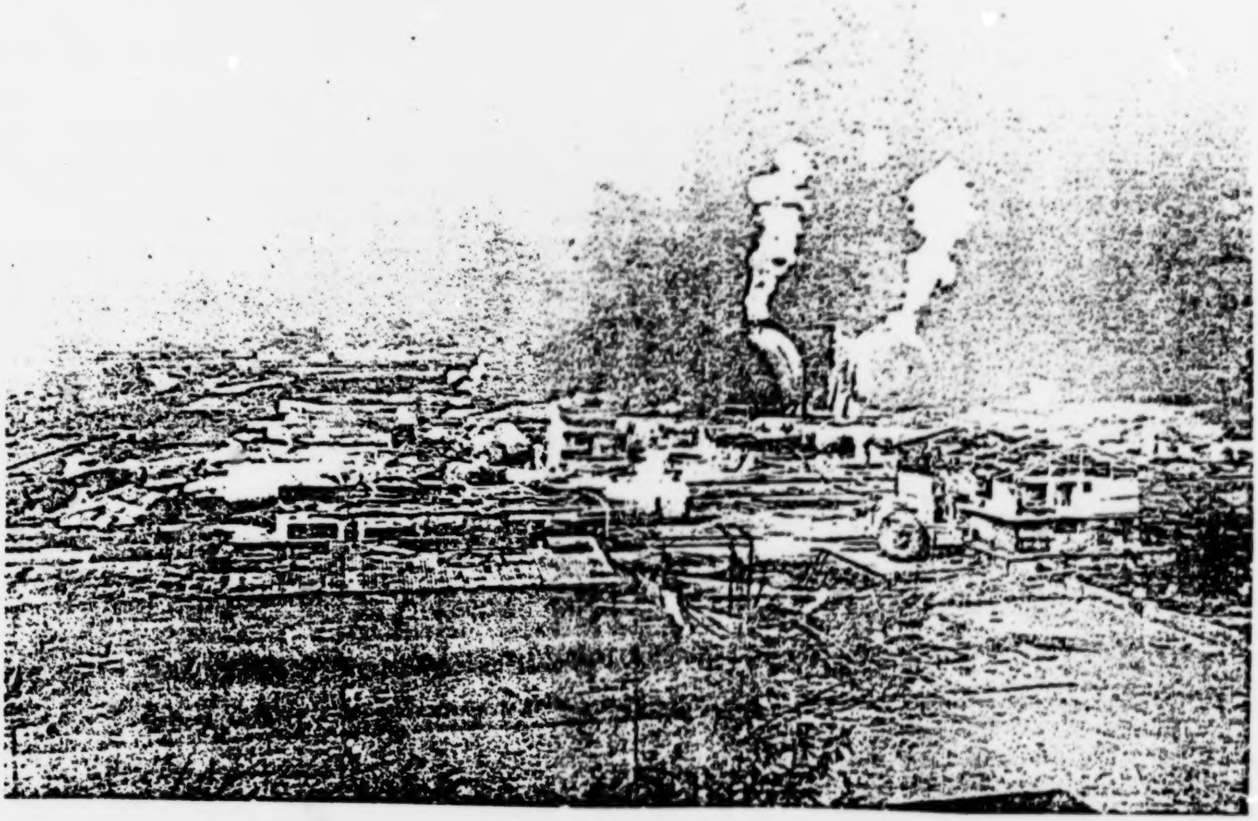


Fig 3 San Juanico(6)

temperature above the boiling point of the other. For example, experiments have been done with LNG (liquified natural gas) and water. When LNG is spilled on a pond of water, the LNG vaporizes and explosive effects are seen.(10) There are also many examples of foundry accidents where molten metal is spilled and comes in contact with water with explosive consequences. In nuclear accidents, the fuel melts due to high temperatures in the reactor. The molten fuel then contacts the cooling water, as in a foundry accident except everything is contained inside the reactor vessel. These are explosions due to boiling liquids. They are not BLEVEs because the term BLEVE is defined for a specific type of boiling liquid explosion, that in which boiling is due to a breach of containment.

It is from this field of research however, that theories about BLEVE mechanisms began. RC Reid(11), when working with superheated liquids, noted that there is a maximum temperature to which a liquid can be superheated. He named this maximum temperature the superheat temperature limit, T_{sl}.

T_{sl} is measured experimentally with two immiscible liquids. A column with the less volatile liquid is heated with a coil such that a temperature gradient exists across the column, with the bottom being cooler than the top. A drop of the other liquid is inserted in the bottom of the column. This small drop is watched as it rises. When it reaches a certain temperature, it explodes with a 'pop'. This temperature is the superheat temperature limit. It can also be calculated from the P-V-T equation of state by setting dP/dV at constant T equal to zero.

One of the theories about liquid-liquid explosions is based on this temperature. It states that the interfacial temperature between the two liquids must be above this T_{sl}, otherwise the boiling is not fast enough to cause a shock wave.(12)

As the temperature of a saturated liquid is increased it should start to boil. This will only happen if there are nucleation sites within the liquid. (See figure 5) Otherwise, it will superheat before it starts to boil. In the case of a BLEVE, at the instant containment is broken the liquid will be superheated relative to the new condition of atmospheric pressure. If the saturation temperature of the liquid before the vessel rupture is much higher than the atmospheric boiling point, then a vapour explosion will occur. How high is 'much higher'?

It is known that when a liquid attains its superheat limit temperature, spontaneous homogeneous nucleation begins and this resembles an explosion.(11) It is possible, then, that for a BLEVE the necessary temperature of the liquid in the tank is T_{sl}. A locus of superheat limit temperatures can be plotted for various pressures, as it is for propane in figure 4. As the fluid is heated from points A to B, it follows the saturation curve. If containment is lost at B no BLEVE will occur because in the isothermal expansion to atmospheric pressure the superheat temperature limit locus is not crossed. However, if the vessel opens at point C, expansion to D will result in an explosion because the liquid would have been able to achieve its T_{sl} as it expanded. The liquid would have had to pass through the superheat limit locus.

For propane, the atmospheric T_{sl} is 53° C (16.5 bar). The conclusion that can be made from the above theory is that there is a safe condition for the storage and carriage of any liquid. If the pressure in the tank can be kept below the saturation pressure T_{sl}, then a BLEVE will not occur if containment is lost. For propane, this would mean a PSV correctly sized and set below 16.5 bar.

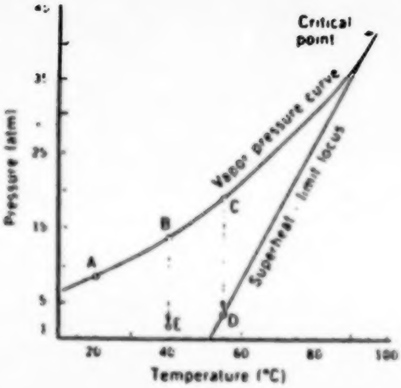
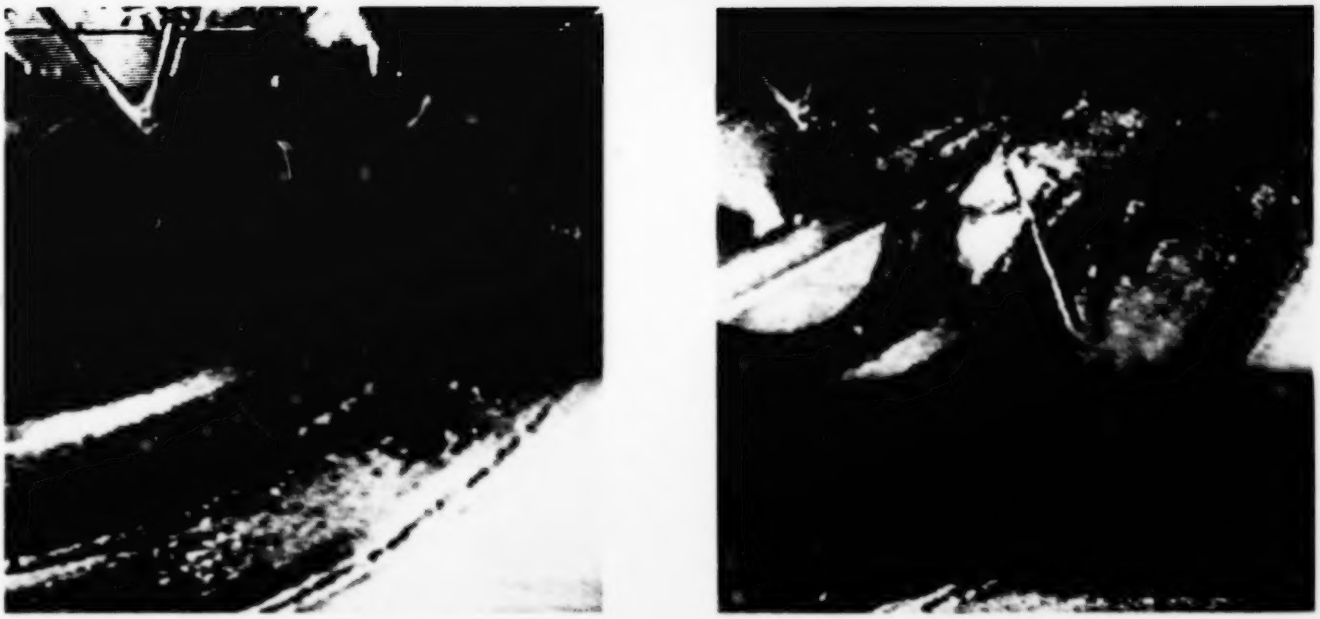


Figure 4: Vapour pressure and superheat curves for propane(12)

Another theory on liquid-liquid explosions comes from the nuclear industry. Board and Hall(13) postulate that as the vapour which is formed at the hot-cold interface collapses it causes a shock wave which in turn causes fine mixtures of the two fluids. In the case of a BLEVE this would mean that when the liquid droplets are sucked into the hot vapour or hot atmospheric air (heated by the fire) a vapour blanket is formed at the interface. As the droplets move through the gas, the vapour blanket is stripped off. Since the blanket was acting as an insulator, there can now be rapid heat transfer between the two phases. The rapid vapourization is the explosion.

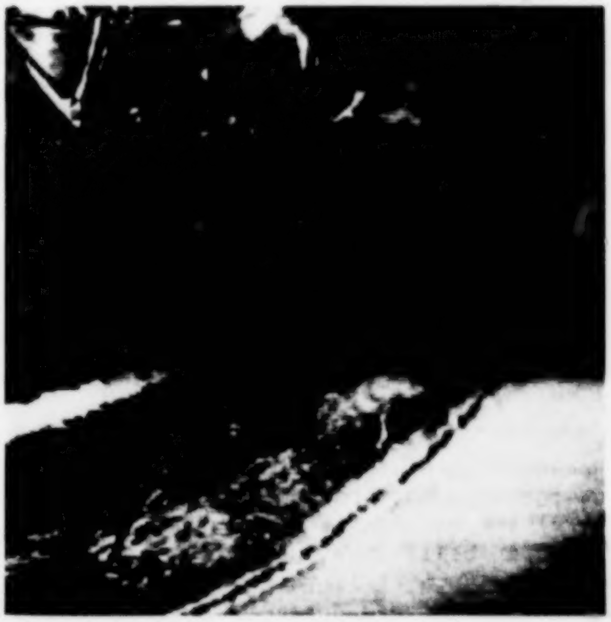
When the vessel ruptures droplets of liquid are sucked into the vapour space (see figure 6). A possible scenario is that with the heat transfer between the liquid droplets and the vapour these droplets will be above the superheat temperature limit and their vaporization may cause the explosion. This theory is similar to Reid's except that it is not necessary for the bulk of the fluid to be above T_{sl}, only the liquid droplets when they contact the hot vapour inside the tank.

The most spectacular and devastating event surrounding a BLEVE of a flammable gas is the accompanying fireball. The fireball usually causes more damage than the blast effects, and rocketing tank parts can trail flaming fluid. It is for these reasons that to some authors a fireball has been mistakenly incorporated into the definition of a BLEVE. In fact, D Lewis(14) has suggested that the definition of a BLEVE be changed to include the fireball. This would have dangerous consequences because the explosion possibility of non-flammables might be overlooked. It is not true that only flammables can explode under the BLEVE scenario. Since it is a physical explosion, the chemical properties of the fluid are not a factor. This question is discussed by W Walls, one of the originators of the term BLEVE, in his paper "Just What is a BLEVE?".(2) It is important that fire fighters and those involved in the transport of liquids are aware of the explosion potential, regardless of the flammability of the fluid involved.



(a) (b)

Fig 5 a-c: Boiling initiating at nucleation sites



(c)

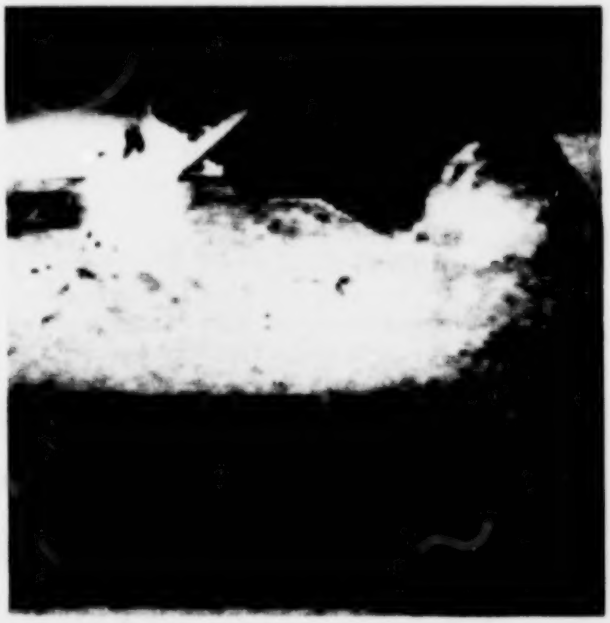


Fig 6: Droplets in vapour space

DISCUSSION

The accident at Crescent City is a perfect example of a typical BLEVE. The tank car was engulfed in a fire, which heated the contents until they were saturated at the relief valve pressure and the relief valve was operating. The flame impingement on the vapour space of the car weakened the metal and caused a tear. The fluid boiled rapidly due to the expansion to atmospheric pressure, and this set up a shock wave. The relief valve was set higher than the maximum as suggested by Reid's theory so that the bulk liquid would have passed through the superheat temperature limit.

The Kingman incident is somewhat different. The flame was only contacting the tank car at the top near the dome. Therefore, the bulk fluid would not have been heated to saturation in the 40 minutes before the explosion. Since the PSV was relieving, the top layer of the fluid was saturated and boiling and there was likely a temperature stratification in the bulk of the fluid. Ambient temperature was 40° C. It is possible that the bulk liquid was raised the necessary 13° C for a Reid-postulated explosion (the T_{sl} for propane is 53° C). The vapour space was certainly above T_{sl} so that any liquid droplets sucked into this area could be superheated. Therefore there is not enough data about this incident to support or invalidate any of the theories about BLEVEs.

At Los Alfaques, the fluid involved was propylene. Since there was no relief device on the truck, it is not possible to determine the internal pressure or temperature at the time of the explosion. It was, however, soon after the fire at the base of the truck. Containment was almost certainly lost because the overfilled truck became liquid full as the fluid heated and the vessel was weakened. It is also entirely possible that after some of the fluid had burned off from the leak in the tank car the vapour was ignited and a chemical explosion occurred. Since the explosion was such a short time after the initial fire, it is doubtful that the bulk liquid or the vapour space were above T_{sl} but again there is not enough data to come to a conclusion about a BLEVE mechanism.

At San Juanico (or San Juan Ixhuatepec) there were two container failure incidents of note that do not fall into the typical BLEVE scenario. Firstly, the most violent explosion was 1 minute after the initial vapour cloud explosion. This was the explosion of one or two of the 1600 m^3 storage tanks. Secondly, one or two of the 2400 m^3 tanks were torn open at the top, with no explosion.

It is not possible that in 1 minute the contents of the spheres would have been heated much above ambient temperature, which was 7° C. The authors of the TNO report(6) on the incident suggest that this first container explosion was a BLEVE and that the mechanism was that of an expanding vapour explosion. (Energy for the explosion is derived from the expansion of a gas from its contained pressure to atmospheric.) This model underestimates the observed damage. They also calculate the damage that would occur with a flash evaporation model which overestimates the damage. It must be noted that the volume inside any of the spheres at the time of the accident is not known, and 50% is assumed by the investigators. A third possibility that was not mentioned at the time is that of a chemical explosion. It is feasible that LPG vaporized and formed a cloud, which was ignited. A comparison of peak overpressure for this case and the two models in the TNO report is shown in Table 2. A chemical explosion shows peak overpressures slightly lower that for a flash evaporation. The possibility of a chemical explosion is not then inconsistent with the damage at the site. The comparison with actual damage is difficult because the volume of the propane in each tank is not known. If there was a chemical explosion, not all of the contents of the tank need be involved, which would lower the overpressure distances.

If the first explosion was actually a BLEVE in the correct definition of the term, then Reid's theory would be discounted. It is not possible that the bulk liquid achieved T_{sl} in that time frame. The fact that at least one of the large spheres was burst but did not explode is significant. There was obviously not enough heat for a rapid boiling to cause a BLEVE when the tank burst. The PSV on the large vessels were set to 11.3 bar, which is below that recommended by Reid. This lack of a BLEVE at these conditions would tend to support Reid's theory.

The Chernobyl accident is not really a BLEVE. The steam was heated to such a high pressure that the reactor could no longer contain it. This incident is included in this paper because of the similarities with a BLEVE and because the theories associated with this type of nuclear accident can be applied to a BLEVE. It is theorized that after the fuel becomes molten it fragments and mixes with the cooling water. Heat transfer is fast due to the high surface area available because of the fragmenting. This leads to the possibility that in a BLEVE it is not the bulk conditions which are a factor but the droplet conditions of the liquid as it is sucked out of the tank car.

TABLE 2

	OVERPRESSURE, bar		
DISTANCE, m	(1)	(2)	(3)
10	2.3		2.7
26		3.0	2.2
50	0.23		0.95
56		1.0	0.78
100	0.09		0.28
120		0.30	0.27
200	0.033		0.18
260		0.10	0.15
560		0.03	0.065
940		0.01	0.035

(1) Vapour Expansion Model(6)
(2) Flash Evaporation Model(6)
(3) Vapour Cloud Explosion Model
All calculation based on the method as described in Baker(15), for a vessel with a volume of 1600 m^3, 50% fill, burst pressure 13.5 bar

RESEARCH AT THE UNIVERSITY OF NEW BRUNSWICK

As previously mentioned, if Reid's theory that the bulk temperature must be above the superheat temperature limit for a BLEVE is true, then BLEVEs can be prevented with PSVs. To test this, we propose to breach containment of small cylinders. These cylinders will be at various measured temperatures. Initially, we will use propane cylinders but we intend to test various fluids

- particularly non-flammables.

So far there have been mentions of correctly sized PSVs, as if this were a simple procedure. Standards for PSVs in LPG service call for vapour relief sizing. In many transportation accidents, the tanker is overturned and the valve will be relieving either a liquid or a two phase mixture. In these cases, a PSV sized for vapour relief will be undersized and will allow the tanker to overpressure.(16) Research done by RA Doyle(17) and K Sumathipala(18) at UNB has shown that when the vapour space is not vented the gas stratifies and extreme temperatures can be measured at the top of the tank. This condition aids in the loss of containment in a fire as the metal is weakened by high temperatures from within as well as without. Work is being done on the redesign of PSVs that will possibly relieve gas independent of tank orientation.

CONCLUSION

BLEVEs can occur in any liquified gas or pressurized liquids, regardless of the flammability of the fluid. Accidents to date do not either prove or disprove any of the current theories. Possible explanations of BLEVEs which involve droplets or small scale events can only be proven by laboratory testing as not enough information of this type is available from an accident. No one measures interface temperatures during a train derailment and fire. The most spectacular incidents happen with flammable gases, and in these cases it is often not possible to rule out that a chemical explosion caused the damage not a physical BLEVE. The term BLEVE has often mistakenly been used in place of the word explosion when dealing with a flammable liquified gas.

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A NEW GENERATION OF SPILL MODEL

Donald Mackay   David Wilson
Department of Chemical Engineering and Applied Chemistry
University of Toronto

ASTRACT:

Chemical and oil spill modelling has reached a state of limited development - it is in the scientific doldrums. The simple, easily understandable models do not treat all the important processes and may thus give misleading results. The more comprehensive, complex models can only be understood by the developer. They may contain errors buried in the mass of undecipherable computer code. Neither is satisfactory, but it is not clear how the situation can be improved.

It is suggested that a new generation of spill models may be on the horizon which are simple but comprehensive. At any given stage in the spill history, only a few of the many possible flow, transfer and reaction processes are important. Rather than include descriptions of all processes at all times, the user would be able to select and include the important processes, but is advised as to which processes are likely to be most important. As the spill progresses, the user is able to intervene to change the selection of processes. It is thus possible to include descriptions of events which occur at specific times such as changing environmental conditions (eg. windspeed or temperature), countermeasures, interactions with shorelines, penetration into soils of differing properties and interactions with ice. The conditions of the spill can be adjusted to agree with actual observations.

The principles underlying this new model approach are described.

INTRODUCTION:

The past two decades have seen heightened concern for our environment and for the effects of chemicals on human health and well being. This awareness and concern, brought about, in part, by a number of chemical spill disasters, has resulted in a new wave of scientific and technical thought. Not only is the production of chemicals and energy and mineral resources accepted as important but the safe transport, disposal and utilization of such chemicals is also seen to be essential. Consequently, the prevention, and prediction of the behaviour of chemical spills has come to the forefront of chemical technology. In turn, the development and deployment of computer models in order to predict the behaviour of chemicals spills, and hence facilitate assessment of effects, recovery or countermeasures has been of growing importance.

The early spill models were simple and consisted largely of algebraic or simple ordered differential equations for such phenomena as flow, evaporation, diffusion or spreading. While these models were useful as approximations of chemical behaviour they were found to be severely lacking in terms of actual applicability to the real situation. The main shortcomings of such models were their inability to account for variations in environmental conditions let alone complete reversals of trends in weather. Also, the early models usually treated only a few of the many physio-chemical phenomena that the spill actually experiences. Hence, they suffered from the very feature that was intended to be their strength; simplicity. Their ease in formulation, comprehension and use was offset by their lack of accuracy in predicting spill behaviour as well as their inability to account for dynamic environmental stimuli.

The early models, while not entirely satisfactory, accomplished the very important goal of initiating well thought out modelling of chemical spills and effectively laid the groundwork for later, more complicated models. This second wave of models attempted to overcome the problems inherent in the simple models. Large quantities of environmental and geographical data were combined with complex analytical and numerical techniques for predicting chemical behaviour. However, while the simple models were too general to predict spill behaviour accurately, the complex models were either too site -specific or too situation-specific. Also, even if the spill actually occurred under the conditions or at the locations specified in the model, the model itself would likely be far too complex to permit its rapid and efficient use. While many of the analytical techniques used in such models were quite innovative and perceptive, it was often only the designer of such a model who was capable of using them. Although these complex models overcame the gross oversimplifications of their predecessors they still, for the most part, were rarely able to cope with dynamic environmental conditions. As it is the very nature of our environment to be variable this factor was and remains the single most important facet of any model of chemical spill behaviour. Further, the models often suffer from an inability to be adjusted when running to include available information about their present conditions, that is they can not be updated.

Thus, the present state of chemical and oil spill modelling has reached one of limited development, caught between the choice of oversimplicity or overcomplexity. The lesson to be learned from the previous work on models is that the key to a successful model lies in how easily and how often it can be used. That is, the ideal model must be simple enough that any number of people can use it effectively and efficiently for a large number of spill situations, encompassing changes in spill as well as environmental status over the course of the lifetime of the spill. One proposed solution is the expert system similar to those that have been implemented for diagnosis of diseases or location of mineral resources.(1) The ideal expert system would require a massive data base describing the likely behaviour of any chemical under any environmental condition in any location. Such a system would be user interactive with the user inputting all available spill and environmental data. The expert system would be programmed to predict spill behaviour based on available input and then specify further data requirements necessary to refine its prediction. The advantage of an expert system over a knowledge based system is that the expert system weighs the relative merits of a number of possible correct solutions and provides a level of accuracy for each solution. In addition a true expert system "learns" from previous decisions it has had to make. A purely knowledge based system requires a match of inputted data with the data or scenarios programmed into the system and is incapable of making a prediction based on an incomplete set of data. However, a complete expert system requires prohibitively large quantities of computer storage space, time and money to develop. Many of the expert systems presently in use in other fields have cost millions of dollars and have required many years to develop. There is also the added drawback that there are a limited number of computers that would be capable of running such a complicated program.

A compelling case can, however, be made for developing a hybrid of traditional and expert systems that contains many of its advantages while avoiding some of the major difficulties inherent in an expert system, namely the unwieldy nature of such a model and the difficulty in developing it. This "new generation" of chemical and oil spill model could be run on a small personal computer and would be user interactive. It would consist of a number of spill descriptions or characteristics such as spill area or thickness as well as physical/chemical characteristics such as density, viscosity or surface tension. In addition, the model would also include the relevant spill processes or events and their respective governing equations. This would include such processes as evaporation, spreading or dissolution. Hence, by the co-ordination of spill descriptions with the particular spill processes that effect them, a chemical spill and the changes that it undergoes may be modelled. By allowing the user to choose which processes to consider, and by updating the status of the spill over time, the model becomes dynamic and thorough without loss of ease of use.

As an analogy one might consider the passage of a canoe across a wide, flowing river. To model its voyage one would include the system's descriptions or characteristics such as the strength and weight of the canoeist, the location of the boat in the river and the wind and current speeds. Then, by choosing the relevant system processes such as drift due to water current or wind and knowing quantitatively how they affect the system characteristics the user may effectively predict the status of the canoe and paddler at any given time. A set of algebraic governing equations would be compiled which would express the net movement and change of status of the canoe due to each process over a selected time increment. For example, on a calm day the user may not wish to consider drift due to wind as a system process but if the river had a strong current he would consider drift due to current. The model would calculate the effect of this process, as well as any others deemed relevant by the user, on system characteristics such as the strength of the paddler and the position of the boat in the river. If the wind became a factor part way through the voyage, the user could then include it as a system process at the appropriate time. Hence, by constantly updating the system descriptions over a particular time segment the user is actually adapting the model to the dynamic nature of the system.

FATE OF SPILLS

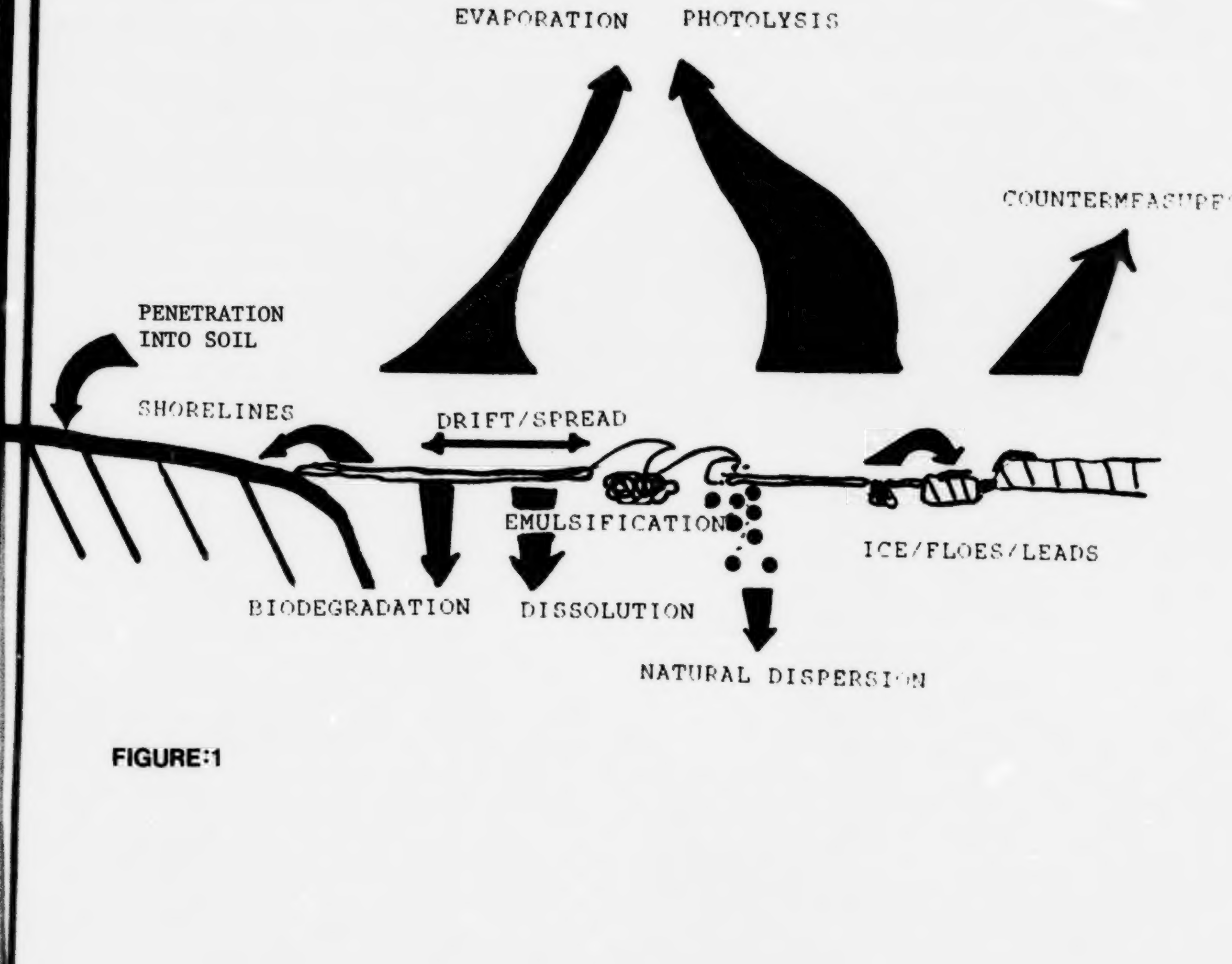
EVAPORATION
PHOTOLYSIS
COUNTERMEASURES
PENETRATION INTO SOIL
SHORELINES
DRIFT/SPREAD
EMULSIFICATION
ICE/FLOES/LEADS
BIODEGRADATION
DISSOLUTION
NATURAL DISPERSION

FIGURE 1

MODEL THEORY AND STRUCTURE:

The focal point of this model is its usage of a time segmented basis which allows the user to specify the relevant environmental conditions and physical/chemical processes applicable to the spill. Also of importance is its "compartmentalized" approach which allows for simple but comprehensive coverage of spill behaviour. By allowing for simple sub-models or governing equations for each spill process the user can treat each process independently. Because the program is user interactive on a time segment basis, the user could update spill conditions after each specified time segment and hence, in effect, track the spill's dynamic behaviour by looking at each process to determine its immediate applicability. In addition this model would also be able to accept a more complex model for any particular process compartment should such a site or situation specific model exist. Such adaptability allows the model itself to improve over time.

This "new generation" of spill model operates on a simple mass balance basis. The chemical spilled has defined physical and chemical properties such as density, viscosity, vapour pressure and solubility. Physical features of the spill such as spill volume, area, thickness, mass and location are also defined. Such properties are considered to be descriptions of the spill itself. A complete set of descriptions would define all desired knowledge of the spill at any given time. A spill which is a mixture of pure components would have each component treated separately with regard to the above properties but summed together to calculate total spill volume, density, thickness, etc.

A list of processes or phenomena which could affect the spill properties or descriptions is also assembled. Processes such as evaporation, spreading, biodegradation, photolysis and if the spill occured on water, dissolution, emulsification, drifting or interaction with shorelines or ice, would be considered with regard to the properties affected. In turn each process's effect on each property or system description must be represented by a governing equation. In most cases the effect of a certain process on a certain property may be calculated with a simple algebraic expression and many of the processes have no effect on many of the properties. For example the evaporation equation affects volume but not area. Spreading affects area but not volume. However the model requires governing equations to treat all of the process/property combinations that could possibly occur.

Initially, the program requests all of the relevant spill data including physical and chemical properties of the material spilled as well as the quantity spilled or rate of release of the material. The program would then request the magnitude of time segments to be considered as well as which processes are to be considered. For each process additional information may be requested in order to satisfy the governing equation. For example, if the spill occurred on water and the spreading and drifting processes were to be considered, the program would request information on wind and water current velocities. Similarly, for evaporation the program would request specific atmospheric conditions in that area. The program would calculate the effect of the designated processes, over the alotted time segment, and update the values of the relevant properties as well as perform a mass balance on the chemical. New values for volume, thickness and area of the spill as well as new density, viscosity, etc. are assigned to the spill. The program would then ask which processes are to be considered for the next time segment, including any new processes to be considered or any to be neglected. There is a possibility that some of the calculated values for each property may by contradicted by actual observation of the spill at any time during the spill. Consequently, after each time segment, the program will request any changes in any properties to be inputted so as to agree with actual observations. By inquiring about new processes to be considered the program could account for countermeasures which may be initiated at some time during the course of the spill. That is, if some of the spill was recovered, dispersed or removed in some way, the resulting change in spill mass or volume would be included in the mass balance.

Thus, by choice of an appropriate time increment, the spill may be monitored and modelled even as the characteristics of the spill change. However, it may be desirable to guide the user who may lack knowledge of what processes are likely to occur in different spill situations. Hence, at the onset of the program general information on the nature of the chemical and the spill itself is requested. For example the program would inquire about the volatility of the chemical, whether the spill occurred on land or water, in a warm or cold climate, or whether the spill was a sudden discharge or a continuous flow. The program could then suggest which processes are likely to be the most important and which are not likely to be a factor. This would still allow the user to include a process, which was initially negligible, at a later time should it eventually become important. It is also possible that the user may lack knowledge of what an appropriate length for a time segment may be. To aid the user the model would be programmed to recognize that certain processes tend to occur more rapidly than others. For example, if a chemical is very volatile then evaporation would tend to occur very rapidly although other processes such as biodegradation may occur much more slowly. By calculating appropriate time segments for each process in the program, the user need only identify which processes he wishes to consider. The program would recommend the shortest approximate time segment from the processes being considered should the user request it.

As an example let us consider a hypothetical spill of oil on water. The user of the program would immediately gather as much information on the spill as possible. At the onset of the program it would ask for as many of the spill descriptors as are available. The user knows that 1000 tonnes of bunker C crude oil were spilled and the slick has been observed to have an area of 1 square kilometre. He also knows from the bill of laiding that this oil has a density of 950 kg/m3. The program requests and receives this information and when the user cannot supply either the viscosity or surface tension of the oil the program suggests approximate values and registers them on file as part of the spill description. The program then asks which processes the user wishes to consider. Since the spill occured in the Arctic, some distance from a land mass, the user chooses evaporation, drifting, spreading and natural dispersion. Upon the user's request the program suggests the shortest approximate time segment from the chosen processes which is that for evaporation and is 12 hours. The program then requests additional information necessary to calculate the effects of the processes on the spill properties. For drifting the program requires wind and water current velocity and direction. Wind speed is also necessary for evaporation and natural dispersion. For a time segment of 12 hours the program then calculates the new spill properties and outputs them to the user.

However, over the 12 hours the spill has moved fairly close to land and is also threatening to come in contact with developing ice. Before initiating the next time segment the program asks if any new processes are to be considered. The user indicates that interaction with a shoreline and with developing ice are now relevant. The program also asks if any of the previously outputted spill properties are to be changed. The user has a satellite report that the spill area is only 85% of that predicted by the program and alters this descriptor accordingly. The program adjusts the mass balance to accomodate this change and requests information for the new processes to be considered. After verifying that the same time segment is to be used the program calculates the new spill characteristics as affected by the relevant spill processes.

During the next time segments some of the oil is removed by skimming while the remaining oil moves away from land and ice. The new processes are added while the ones no longer relevant are removed. This series of modelling steps may continue as long as required and allows the user to chart the evolution of the spill as it occurs and becomes subject to a variety of processes.

MODEL EQUATIONS:

The entire success of this model is dependent upon the accuracy of the individual process equations. As already indicated it is not desirable to have governing equations that are too site -or too situation- specific, nor is it desirable to have equations that are so general that they provide very little indication of the true behaviour of the spill. This stipulation makes the choice of governing equations somewhat subjective. However, the nature of this model, which is to allow for replacement of governing equations or submodels or modules as superior ones are developed, provides flexibility in choice of governing equations as well as ample opportunity for improvement. Figure 2 illustrates some of the possible spill processes and the spill characteristics they are likely to affect.

A number of governing equations have been compiled and are presented here by the authors which are considered to be satisfactory initial governing equations for this model. We expect that better equations will be proposed which may be superior in a given location or situation.

BIODEGRADATION:

Biodegradation is a process which probably has a situation specific rate dependent on the temperature, oxygen and nutrient availability and status of the microbial community. However, it is believed that a simple, first order exponential decay equation appropriately describes the decrease in mass or volume of the chemical, due to biodegradation, with time. This governing equation would have the form of:

$Mi = Mio \exp(-kt)$ where

Mio = initial mass of chemical
Mi = mass of chemical at time (t)
k = degradation rate constant specific to the chemical
t = time increment (in days)

Use of this equation assumes no changes in the properties of

MODEL EVENTS

PROCESSES

DESCRIPTORS	EVAPORATION	DISSOLUTION	DISPERSION	BIODEGRADATION	PHOTOLYSIS	EMULSIONS	DRIFT	SPREAD	SHORELINES	SLUSH	COUNTERMEASURES
Volume	●	●	●	●	●	●			●	●	●
Area					●			●	●	●	●
z	●	●	●	●	●	●		●	●	●	●
μ	●	●		●	●						
ρ	●	●		●	●						
v.p.	●	●		●	●						
Comp.	●	●		●	●						
Loc.							●				

FIGURE:2

(z = thickness)

the non-degraded chemical and accounts only for loss of mass of chemical due to degradation. This equation requires knowledge of a degradation rate constant or half-life. This information will probably not be readily available for some chemicals. Consequently, the program would suggest a range of half-life times for various classes of chemicals that may be used when actual values are not known. For example, normal alkanes are thought to have half-lives of approximately 50 days. Alcohols may have a shorter half life of 10 days whereas aromatic compounds usually have degradation half lives on the order of 60 days and isoprenoids on the order of 300 days.

EVAPORATION:

Evaporation is one of the most important processes that is likely to occur to a spilled chemical and is especially important for very volatile chemicals. A useful method of treating the evaporation process involves the consideration of the "evaporative exposure" of the chemical as proposed by Stiver et al.(2). For pure liquids, such a governing equation takes the form:

$Fv = H\,Q = (Pv/RT)(kat/Vo)$ where

Fv = volume fraction evaporated
H = Henry's Law constant for chemical
Q = evaporative exposure
P = chemical vapour press.
v = chemical molar volume
R = ideal gas law constant
T = temperature
k = mass transfer coeff.
a = spill area
t = time evaporating
Vo = initial spill volume

As with biodegradation, this form of equation requires knowledge of the mass transfer coefficient and some of the physical properties of the chemical, specifically the vapour pressure at a given temperature. Again, the problem of lack of this knowledge is avoided by suggestions, by the program itself, of appropriate ranges of values for these properties, for different classes of chemicals. This information would be based on known correlations for mass transfer coefficient as a function of wind speed. Also, because the chemicals are assumed to be pure, the physical properties of the unevaporated chemical are assumed to remain unchanged. Chemicals are also assumed to evaporate uniformly across the surface of the spill.

SPREADING:

Knowledge of rates of spreading of chemicals is also instructive for prediction of spill behaviour. Work has been performed on spreading of chemicals on land by Kawamura (3) and spreading on water by Mackay et al.(4). The Mackay model requires knowledge of three spreading constants as well as initial spill volume, thickness, area and release rates. The constants can be estimated by correlations derived in (4) and again the user of the program would be guided as to the choice of the value of the constants, dependent upon the class or type of chemical spilled.

DISSOLUTION:

If the spill occurs on water, dissolution of the chemical may be quite important. A simple equation to estimate the quantity of chemical lost through this process takes the form:

$$M = ak(Csol - Cw)t$$

where

M = amount of chemical which is lost to water (mass)
a = spill area
k = mass transfer coeff.
$Csol$ = max. conc. of chemical in water as dictated by solubility of chem.
Cw = actual chem conc. in water (assumed close to zero)
t = time increment

In a large body of water the actual chemical concentration in water is always low because of the large volumes of water involved and hence the concentration driving force approaches the solubility concentration limit itself. Again, a mass transfer coefficient is required and guidance to the user from the program will be offered.

DRIFTING:

For drifting of a spill on water it is generally accepted that drift velocity will be approximately three percent of the ten metre wind velocity. Hence actual drift velocity and direction may be obtained from the vector sum of water current velocity and 3% of the 10 metre wind velocity.

OTHER PROCESSES:

There are also equations available for natural dispersion of chemicals in water, emulsion formation and interaction of chemical spills on water with shorelines, ice, etc. For possible countermeasures to a spill it is assumed that the user will have knowledge of the percentage of a spill that a particular countermeasure is expected to remove. Thus, that particular mass or volume of chemical could be removed from the program s mass balance on the chemical.

An area where a satisfactory governing equation has yet to be derived is photolysis of chemical spills. For such a process the user will not have the option of including the process in his spill behaviour scenario. However, as previously mentioned, should an appropriate governing equation be arrived at in the future it may be included in the model.

DISCUSSION:

Although this "new generation" of spill model has the great advantages of simplicity and the capability to interact with the user, its greatest asset may be its own adaptability and flexibility. While conventional models immediately begin to be outdated upon their very completion this new form of spill model can evolve with changing modelling techniques. That is, the "compartmentalized" or "modular" form of this type of model allows for any of the governing equations or submodels to be replaced by more accurate or convenient governing equations or submodels, as they are developed. This is the same mechanism that permits the incorporation of site or situation specific submodels in the present form of the model where appropriate. It has already been noted that there are some compartments in this model for which not even simplified governing equations are available. Also, there may be processes, so far considered irrelevant, or new artificial processes, spawned by technological breakthroughs, which it may be desirable to include in the model in the future. This form of model has the advantage that it acknowledges and accommodates the dynamic nature of modelling by allowing for such improvements or alterations in the model itself.

Thus, the distinguishing feature of this model is that rather than relying on new analytical techniques or computer programming methods, it provides a skeleton or framework for existing submodels or governing equations as well as future submodels or processes. It is simple yet comprehensive and adaptable to more complicated submodels.

The future work required with this model consists of improving the program´s "decision-making" ability. That is, expanding the program´s data bank to permit more effective guidance from the program in the user´s decision making process. In effect the program must have built in a broader range of possible spill scenarios to compare to the actual initial spill conditions. In the future it would also be necessary to accumulate as many existing spill submodels as possible and adapt them to the form required for this program. This would allow the user the luxury of choosing between a number of submodels or governing equations for each compartment. The program would be able to advise which of the submodels is superior for a given spill situation. Eventually there would be the capacity for subdivision of the overall model depending upon general geographical location or chemical nature. For example there could be a temperate or Arctic, organic or polar chemical version of the model.

This modelling approach can be regarded as a computer simulation of a situation in which an on-scene commander calculates the change in behaviour of a chemical or oil spill. He has available to him a room of "experts", one on evaporation, one on spreading etc. To predict the spill behaviour he selects a number of experts and asks them, "How will the spill change in the next 2 hours as a result of your process?". The answers will come back independently as for example, "loss of 5% volume" or "spreading by 20%" or "drift of 1 km to the East". These answers will simply be added to give a picture of the new spill situations. The experts will be called upon as needed, but they may intervene to claim that they should be considered or ignored or to suggest a better time increment.

In the program each expert is an equation expressing the change in each descriptor as a funtion of chemical properties, environmental conditions and the length of the time increment. The equation can be pulled out and replaced as better ones emerge, ie the expert can be replaced.

In conclusion, while the model, in its present state of development, contains gaps in information and contains some oversimplifications of physical and chemical processes it provides a method and framework for the creation of a simple, comprehensive model for chemical spills. This model has the great advantage of having the capability to interact with the user to follow the dynamic nature of a spill as well as the ability to follow the dynamic nature of modelling technology itself through contingency for addition of new or improved submodels, governing equations or chemical properties.

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CONTINUED DEVELOPMENT OF A HEAVY GAS DISPERSION MODELLING SYSTEM: COBRA III

E. Alp, C.P. Bourque, M. Oliverio, Concord Scientific Corporation,
D. H. Napier, University of Toronto,
C.H. Matthias, Atmospheric Environment Service

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INTRODUCTION

Increased use of toxic or flammable liquefied gases in recent years as a source of energy or chemical feedstock by industry has pointed to the need for developing and maintaining practical and well-tested heavy gas dispersion models for estimating hazard zones for accidental releases of these chemicals.

In response to these needs, Concord Scientific Corporation with financial support from the Energy R & D Fund, Environment Canada, has developed a heavy-gas spill and dispersion model (COBRA). The original model was designed primarily to simulate instantaneous or constant liquefied (refrigerated) natural gas (LNG) spills on large bodies of water for application to marine-tanker accidents (Alp _et_ _al_., 1985). A second version of the model (COBRA II) included extensions of the original model to: four chemicals, time varying spill rates, spills on land, confined spills, and simultaneous liquid and gas releases (Alp _et_ _al_., 1986). Since the last reporting, several further enhancements were made to the model, the most notable one being incorporation of the ability to handle liquid droplets of the spilled heavy gas liquid (HGL) within the plume. To the authors' knowledge, this latter enhancement, which is essential for modelling releases of chemicals such as chlorine, ammonia and propane from pressurized containers such as storage spheres, or rail or truck tankers, makes COBRA III the only practical model in the world which has this capability. It is the purpose of this paper to present this and other enhancements.

COBRA III presently forms the cornerstone of Concord's Comprehensive Hazard Assessment System for Estimating Risk (CHASER) due to releases of hazardous materials during their manufacture, transportation and storage. This integrated risk assessment system has been and is being used in several hazard and risk assessment studies for transportation (both land and marine) and chemical process industries.

DESCRIPTION OF ORIGINAL MODEL COBRA

Briefly, COBRA treats the gas source, whose size (radius) and gas emission rate have been determined by the pool spread and gas generation module, as a steady idealized rectangular source of equivalent area. Over the source, gravity spread is neglected and a Gaussian concentration profile is assumed in the vertical. If the emitted gas cannot be taken up completely by the wind, which is assumed to have a power law profile, then a pure gas blanket is allowed to form over the liquid pool. This gas blanket also spreads by gravity. Its size, determined in a similar manner to the liquid pool, is, in turn, taken as the size of the gas source. At the downwind edge of the source, the horizontal concentration profile is assumed uniform. This uniform core spreads in the lateral direction under the influence of gravity and turbulent diffusion. The plume concentration distribution at the lateral edges is assumed to be Gaussian. Further downwind, the uniform central core is completely spent and a smooth transition to passive Gaussian dispersion is provided. The treatment of heat transfer and humidity is facilitated through the use of mass and energy balances performed on a vertical slice of the plume perpendicular to the flow direction.

The model also treats transient gas releases, i.e., releases in which the area of the gas source varies with time. This is accomplished by using "observers" which take up gas as they pass over the gas source. A steady state calculation is then made for each observer. By knowing the location of each observer as a function of time, it is possible to determine flammable cloud hazard zones due to contributions from successive "observers" at any desired time.

COBRA requires meteorological information during the release, such as wind speed, stability, air and surface temperature, as well as information on the type (e.g., instantaneous, finite time, continuous) and size of spill, the type of surface (e.g., land, water, open, confined) on which the spill occurs, the surface roughness of the terrain over which dispersion is assumed to take place, and of course the spilled material.

Outputs from COBRA include the maximum hazard zone length, width, and height, and their corresponding times from spill initiation, as well as plots of hazard zones for these times. Hazard zones are based on input hazard limits in terms of volume fractions for the materials of interest.

COBRA is suitable for continuous, finite time or instantaneous releases of heavy-gas-producing liquids and/or heavy vapours. It is applicable to dispersion over homogeneous flat terrain and does not handle flow disturbances due to individual obstructions such as buildings or ridges.

MODEL EXTENSIONS: DESCRIPTION OF COBRA III

In the pursuit of generalizing COBRA's capabilities as a heavier-than-air-gas release and dispersion model, numerous extension modules have been added, resulting in the present version (COBRA III). Since the last reporting of COBRA II (Alp et. al., 1986), the following additions were made to the modelling system: (1) ability to handle HGL droplets within the gas cloud, (2) extension to ammonia in addition to methane, propane, butane and chlorine, (3) incorporation of a source module based on Belore and Buist (1986) and Oliverio (1986), (4) improvements on the structure of the code to decrease computer costs. The modifications related to the first enhancement above will now be described in somewhat more detail.

MODEL CHARACTERISTICS

The discharge of a liquefied heavy gas from pressurized or semi-refrigerated containment will result in a two-phase release. The instantaneous flash fraction, f, can be obtained from an overall enthalpy balance.

Part of the remaining liquid fraction for such releases will be taken up by the vapour in fine droplet form. The remaining liquid will form a pool on the ground as in the old version of COBRA (COBRA II). The distribution of the liquid between fine droplet mist and liquid pool is dependent on (i) the material, (ii) the storage conditions and (iii) the orientation of the discharge jet. For releases of pressurized ammonia, Kaiser and Griffiths (1982) found that virtually all the liquid formed a mist when the jet was oriented vertically upwards. When a jet is directed vertically downwards, impingement of liquid on the ground occurs causing a significant fraction of the liquid to form a pool (Blanken, 1980). Since it is extremely difficult to predict how the unflashed liquid will divide itself between mist and pool, the separation is used as a sensitivity parameter.

The following assumptions were made in developing the model equations:

(1) At a given downwind distance, the plume is homogeneous in the crosswind and vertical directions.

(2) All energy entering the plume will cause liquid heavy gas (LHG) particles to evaporate until they have all evaporated.

(3) A fraction, p_o, of the LHG particles will settle out of the plume over each distance increment and no longer contribute to the plume.

(4) A fraction, q_o, of the condensed water will settle out of the plume over each distance increment.

From these assumptions, the plume can be divided into three distinct zones as shown in Figure 1. In the first zone, suspended LHG droplets evaporate due to heat introduced from the entrained air and heat transfer from the ground. Water vapour entrained with the air will condense and liberate energy. The temperature of the plume is assumed to remain constant at the normal boiling point of the heavy gas.

Transition to zone 2 occurs when all of the LHG has evaporated. At this point, the plume will begin to warm up. As the temperature of the plume increases, water will evaporate until, in zone 3, no liquid water remains in the plume.

The physical characteristics are similar to those used by Colenbrander (1980) in his advanced similarity heavy gas dispersion model, on which COBRA is based. While the plume is heavy, slumping is modelled through a uniform slab of half width, B_{eff}, and height, H_{eff} travelling at an effective volocity, U_{eff}, such that at a downwind distance, x,

$$\rho m\bar{c}\, B_{eff}H_{eff} = \iint c(y,z)dydz$$

The plume centerline ground level concentration is calculated from,

$$C_A = \frac{\dot{m}_{hgv}(1+\alpha)Z_o^{\alpha}}{2U_oS_z^{(1+\alpha)}B_{eff}}$$

From the above concentration and the dispersion parameters, the crosswind and vertical plume concentration distributions are calculated and corrected for x-diffusion.

The steady state model enhancements that have been incorporated into COBRA require that equations for the following be solved simultaneously in order to predict the plume characteristics at a given downwind distance:

- vertical diffusion
- crosswind diffusion
- gravity spread (for B_{eff})
- mass balances for each species
- energy balance
- equation of state
- equilibrium (Clausius-Clapeyron)

In zone 1, the evaporating heavy gas liquid will increase the mass of heavy gas vapor and thus the volume of the cloud. The dispersion parameters will be influenced by this, and it was assumed that the effect is taken into account in the gravity spread equation. This assumption is conservative in both the downwind and crosswind directions. Therefore,

$$\frac{d}{dx}(B_{eff}) = \frac{d}{dx}(B_{eff})_{\substack{\text{gravity}\\\text{spread}}} + \frac{d}{dx}(B_{eff})_{\text{evap.}}$$

Furthermore, when the density of the plume approaches that of air,

$$\frac{d}{dx}(B_{eff}) = 0$$

and slumping ceases.

The diffusion equations were developed from Colenbrander's (1980) theorectical work and remain unchanged from the original COBRA model, except to say that the magnitude of B_{eff}, which is part of both equations, has been modified.

Separate mass balances are written for each species in the plume, i.e. (i) air, (ii) water vapour, (iii) liquid water, (iv) LHG, and (v) heavy gas vapour. Mass is gained through the entrainment of moist air and is lost through the deposition water and LHG particles. An overall energy balance, equation of state and the Clausius-Clapeyron equation form the remaining equations that close the equation set. For the density equation, the liquid particles are assumed to have no volume, contributing only to the mass, such that

$$\rho_m = \frac{\sum_i \dot{m}_i}{U_{eff}B_{eff}H_{eff}}$$

RESULTS

Table 1 shows the maximum hazard zones predicted for several different release scenarios. In general (i) the allowance for liquid mist tends to increase the size of the hazard zone (scenario 2) and (ii) allowing liquid water to remain in the plume (scenario 6), as opposed to dropping it out (scenario 5), also gives larger hazard zones. Both factors have a cooling effect on the plume. These results indicate the importance of the ability to handle liquid droplets within the gas cloud. Figures 2-4 show results on some comparisons with field data.

NOMENCLATURE

B_{eff} = effective plume half width

C_A = plume centerline concentration

$\bar{C}$ = uniform concentration within effective slab

f_l = liquid fraction of heavy gas forming pool

f_m = liquid fraction of heavy gas forming mist

f_v = flashed vapour fraction of heavy gas

H_{eff} = effective plume height

$\dot{m}_{hgl}$ = mass of heavy gas liquid

$\dot{m}_{hgv}$ = mass of heavy gas vapour

$\dot{m}_{wl}$ = mass of liquid water

p_o = fraction of heavy gas liquid which drop out of plume

P_A = ambient pressure

P_{vp} = vapour pressure of the heavy gas at T_A

q_o = fraction of liquid water that drops out of plume

R_m = radius of confinement

S_z = vertical dispersion parameter

t = time

T_A = ambient temperature

T_g = gas temperature

T_{nbp} = normal boiling point temperature of the heavy gas liquid

T_{dp} = dew point temperature

U_{eff} = effective plume transport velocity

U_o = wind speed at reference height

$\dot{V}_c$ = release rate of liquid from tank

X_{max} = size of downwind hazard zone

Z_o = reference height (10m)

ρ_m = plume density

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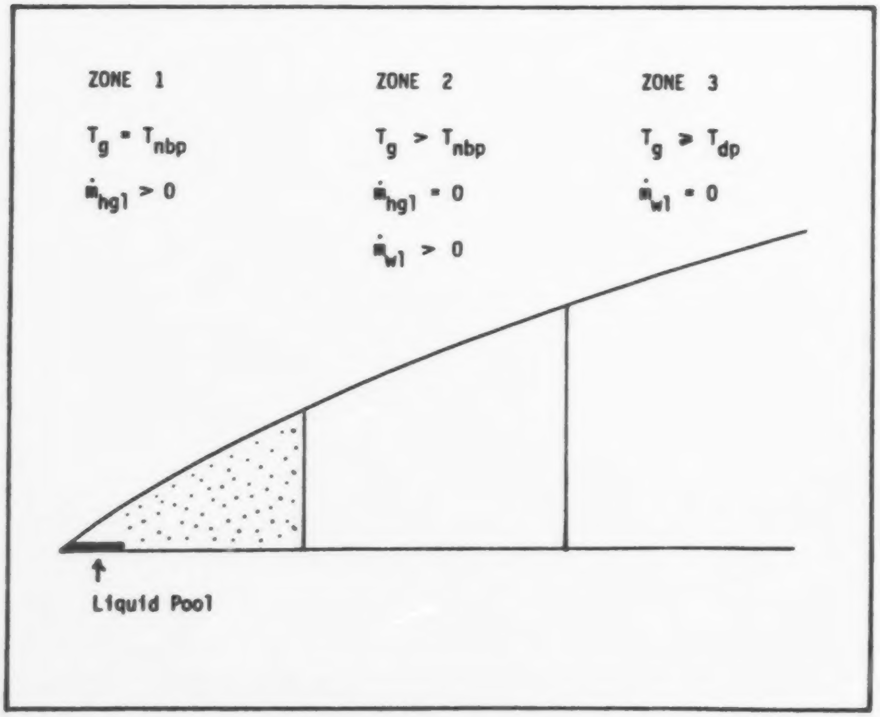
TABLE 1

Scenario	Material	$\dot{V}_c$ (m^3/s)	t (s)	f_1	f_m	f_v	q_o	Confined (Rm in m)	X_{max} (m)
1	Propane	0.033	90	1.0	0	0	1.0	No	185
2	Propane	0.033	90	0.01	0.69	0.30	1.0	No	268
3	Propane	0.033	90	0.14	0.56	0.30	1.0	No	254
4	Propane	0.033	90	0.56	0.14	0.30	1.0	No	162
5	Propane	5.0	100	1.0	0	0	1.0	No	3110
6	Propane	5.0	100	1.0	0	0	0	No	3730
7	Propane	5.0	100	1.0	0	0	1.0	$R_m = 7.0$	92
8	Propane	5.0	100	1.0	0	0	1.0	$R_m = 25.0$	379
9	Propane	5.0	100	0.35	0.35	1.30	1.0	$R_m = 25.0$	1069
10	Chlorine	40.0	1	1.0	0	0	1.0	No	29500

Notes: (1) R_m = Maximum pool radius equals dike radius
(2) T_{air} = 30°C, $T_{surface}$ = 30.1°C
(3) Humidity = 62%
(4) Criteria for X_{max}: Propane = LFL, Chlorine = 15 ppm

FIGURE 1: COBRA III Heavy Gas Plume Schematic Description


ZONE 1
$T_g = T_{nbp}$
$\dot{m}_{hgl} > 0$
ZONE 2
$T_g > T_{nbp}$
$\dot{m}_{hgl} = 0$
$\dot{m}_{wl} > 0$
ZONE 3
$T_g \geq T_{dp}$
$\dot{m}_{wl} = 0$
Liquid Pool

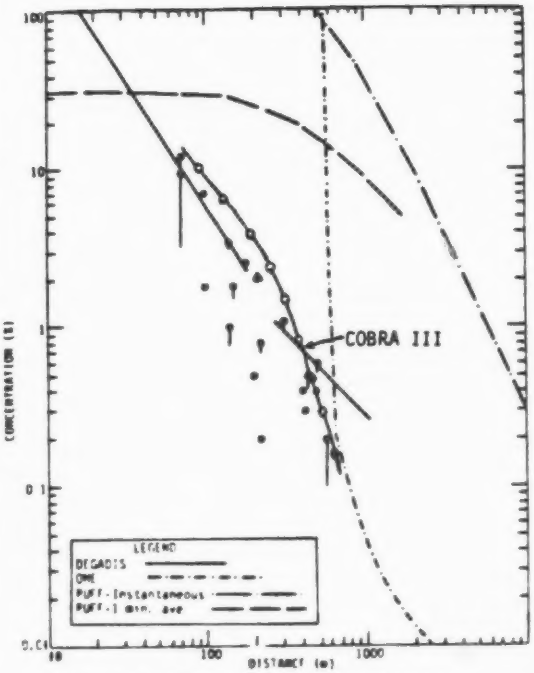


Figure 2. COBRA III model predictions against measured and predicted concentrations for Thorney Island Trial 9 (Layland et. al., 1986).

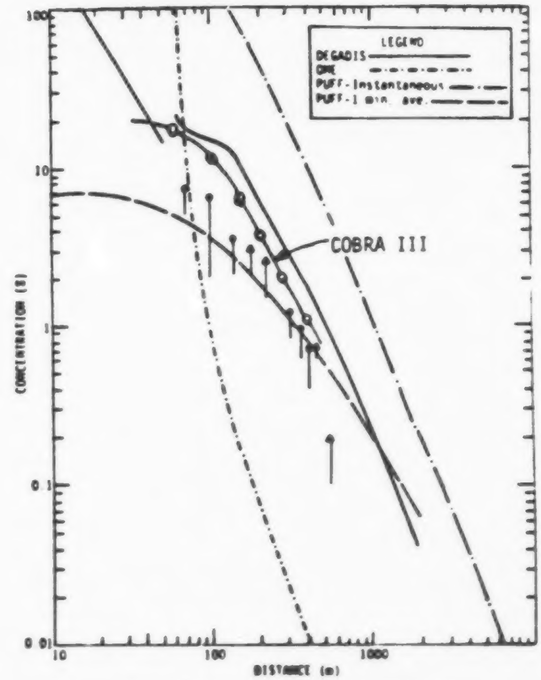


Figure 3. COBRA III model predictions against measured and predicted concentrations for Thorney Island Trial 13 (Layland et. al., 1986).

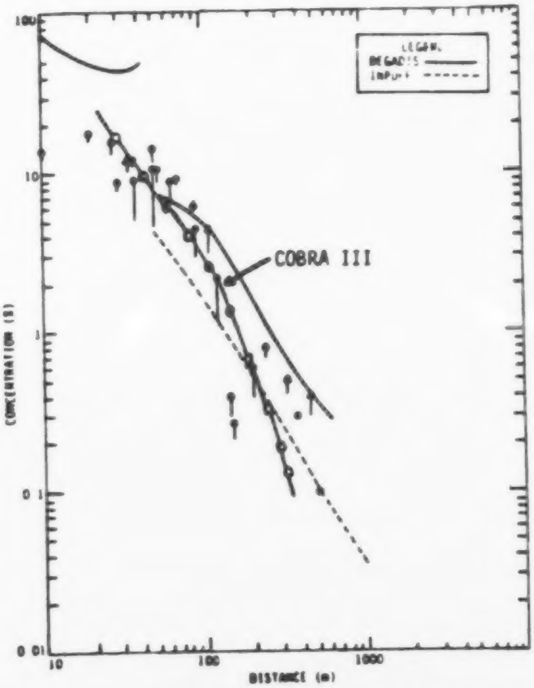


Figure 4. COBRA III model predictions against measured and predicted concentrations for Thorney Island Trial 45 (Layland et. al., 1986).

RESTORATION OF SITES CONTAMINATED BY POLYAROMATIC HYDROCARBONS (PAH'S)

Jean Paquin, P. Eng.

and

Adrien Pilon, Geol., M.Sc. Env.

Technical Services
Sanexen International Inc.

ABSTRACT

RESTORATION OF SITES CONTAMINATED BY PAH's

Several sites have recently been discovered to be contaminated with considerable quantities of tar. The tar located in damaged underground tanks, abandoned dumps and even in river bottoms, and it generally originates from coking or gas production operations; it presents a difficult problem since it often contains important quantities of compounds in the family of polyaromatic hydrocarbons some of which have a carcinogenic potential.

The communication will cover a few case histories and will outline methods used for the handling, treatment and destruction of these contaminants. The following processes will be reviewed: solidification of the viscous semi-liquid tar, ultrasorption for the treatment of contaminated water, and biolysis for destruction of the organic contaminants and detoxification of the waste material.

INTRODUCTION

The decommisionning of industrial sites and the reuse of abandoned properties lead to the discovery of oily wastes and tars leaking from underground tanks or drums, creating a potential for contamination of the surrounding soil and groundwater. These tars and oily wastes sometimes contain important quantities of compounds in the family of polyaromatic hydrocarbons (PAH), some of which have a carcinogenic potential.

This communication will describe the different steps likely occur in the restoration of sites contaminated by PAH's. A brief summary of the physico-chemical and biological properties of PAH's is also be presented. Finally the different technologies available for soil and groundwater decontamination are reviewed.

Two case histories will be explained and will outline methods used for the handling, treatment and elimination of PAH'S.

1.0 SOURCES OF PAH

PAH's occur in the environment from natural sources and industrial sources. (ref: 1 & 2)

Natural sources of PAH's include the products from forest and grass fires, geochemical processes and synthesis by microorganism and plants.

Background levels range from 0.01 to 88 ug/kg in soils, 0.001 to 0.1 ug/L in groundwater and 1 to 10 ug/kg in plants

PAH's also enter the environment through industrial emissions to atmosphere reaching soil and water as particulate fallout. Effluent water has also been a significant mode of transfer of contaminants in some cases. PAH's may also reach soil and groundwater through spillage or disposal of wastes.

Main sources are:

- thermal generating plants
- coke production
- open burning
- petroleum refining

2.0 PROPERTIES OF PAH's

The PAH'S have generally a low water solubility and a high lipid solubility, so they can persist in the environnement and bioaccumulate in organisms. High molecular weight PAH's such as benzo-(a) pyrene are resistant to degradation (volatilization, photolysis, biological) and tend to adsorb to organic matter in soils and sediments. PAH's with low molecular weight show a more acute toxicity than high molecular weight PAH's which have a carcino/mutagenic potential. Because of their high solubility in lipids, PAH's will be found in human and animal adipose tissues and tend to accumulate (ref: 1.4).

The knowledge of properties of PAH's is predominant to establish the restoration of a site contaminated with PAH's. The environmental evaluation includes the characterization of the site during which levels and extent of contamination will be evaluated. General properties of PAH's are presented in the following tables.

TABLE 1
PROPERTIES OF PAH'S[1]

PAH	MOLECULAR WEIGHT	WATER SOLUBILITY (mg x L^{-1})	ACUTE[2] TOXICITY	CARCINO/[2] MUTAGENCITY
Naphtalene	128	31.7	+	-/-
Phenanthrene	178	1.29	+	-/-
Anthracene	178	0.073	?	-/-
Pyrene	202	0.135	?	-/-
Fluoranthene	202	0.260	+	-/+
Benzo (a) anthracene	228	0.014	?	+/+
Chrysene	228	0.002	?	+/+
Benzo (a) pyrene	252	0.004	++	+++/+

[1] Reference 1

[2] From Sims and Overcash, 1983

TABLE 2
CARCINOGENICITY OF PAH'S[1]

SUFFICIENT EVIDENCE OF CARCINOGENICITY FOR PAH'S

Benz (a) anthracene
Benzo (b) fluoranthene
Benzo (j) fluoranthene
Benzo (k) fluoranthene
Benzo (a) pyrene
Dibenz (a,h) acridine
Dibenz (a,j) acridine
Dibenzo (a,h) anthracene
7H-dibenzo (c,g) carbazole
Dibenzo (a,e) pyrene
Dibenzo (a,h) pyrene
Dibenzo (a,i) pyrene
Indeno (1,2,3-cd) pyrene
5-methylchrysene

LIMITED EVIDENCE OF CARCINOGENICITY FOR PAH'S

Anthanthrene
Benzo(c) acridine
Carbazole
Chrysene
Cyclopenta (c,d) pyrene
Dibenzo (a,c) anthracene
Dibenzo (c,j) anthracene
Dibenzo (a,e) fluoranthene
2-Methylchrysene
3-Methylchrysene
4-Methylchrysene
6-Methylchrysene
2-Methylfluoranthene

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[1] From IARC, (1983), reference 4

3.0 ENVIRONMENTAL EVALUATION

Leading to the restoration work, site characterization is necessary in order to design the proper treatment facilities required during the restoration.

3.1 SITE CHARACTERIZATION

The site characterization is done following the different steps listed below;

1. Historical data:
   - volumes of product spilled or otherwise present
   - chemical and physical properties of the products involved
   - location of underground services (tanks pipelines, sewers, etc.)
2. Sampling
   - obtain information about the stratigraphy and permeability of the soils
   - obtain information about the characteristics of the aquifer.
   - Proper material for soil and ground water sampling.
   - Proper number and distribution of samples for statistical validity
3. Analytical program;
   - establish clearly the analytical methods refering to standards (EPA, Environment Canada, MOE, MENVIQ, etc).
   - proper limits of detection to meet regulated levels and for significance of results
   - identification of specific contaminants
4. Clean-up criteria;
   - discussion with authorities to determine the levels of decontamination of soils and water.

3.2 SITE RESTORATION

3.2.1 AVAILABLE TECHNOLOGIES

3.2.1.1 SOIL AND SOLIDS DECONTAMINATION

a) biological treatment
   - land farming
   - biolysis
   - aerated pile

b) immobilization of contaminants

c) excavation and landfilling

d) high pressure cleaning

e) solvent extraction

f) thermal process (incineration)

3.2.1.2 WATER DECONTAMINATION

a) stripping (mainly low molecular weight PAH)
b) microbial oxidation
c) coagulation, flocculation and sedimentation
d) Photo oxidation, UV and ozone
e) filtration, absorption and adsorption

Site restoration involving contaminated soils and ground water requires a combination of different technologies in order to achieve acceptable levels of contaminants in the environment. The choice of the methodologies will be dependent of economic and regulatory constraints.

4.0 CASE HISTORIES

Since 1984 Sanexen International Inc. has been involved in the restoration of sites where PAH's were present. Different technologies were utilized for the treatment of soils, solids, groundwater and sludges; new technologies were also developped and used in some of the cases.

4.1 CASE 1

Restoration of a urban site contaminated with coal tar; treatment of groundwater and disposal of contaminated solids.

4.1.1 SCOPE OF THE WORK

a) decontamination of liquids and solids in underground tanks and groundwater
Contaminated solids; 3000 cu. yards
Contaminated liquids; 50,000 gals.

b) Treatment objectives
- less than 15 mg/ L oil and grease
- less than 1 mg/L phenols
- less than 1 mg/L for PAH

4.1.2 DESCRIPTION OF THE RESTORATION PROGRAM

a) Solids decontamination

- Excavation of contaminated semi liquid tar and solids from underground storage tanks (wood and bricks);
- construction of a drying bed for the temporary storage of the solids; the water drained from the wet solids was pumped to the treatment facility;
- solidification of the semi-liquid sludge with flyash and lime ;
- covering of the stockpiled material with an overliner;
- disposal of the solids in a secure landfill; transport to secure landfill by trucks appropriately tarped.
- segregation and interim storage of material with low contamination levels

b) Water treatment

A well consisting of a 10 feet long by 30 inches diameter perforated galvanized pipe was installed to house submersible pumps and controls. The contaminated groundwater was directed to the water treatment system.

Extraction of PAH's and phenols from water was performed using the Sanexen mobile water treatment system. This system is designed to remove organic contaminants in all form: suspended, colloīdal, emulsified and soluble contamination.

This mobile compact installation is designated as an ultrasorption unit because of the overall high capture efficiency of the system.

Pretreatment was used to remove free floating hydrocarbons and the bulk of the solids. Oxidation of the residual phenols took place after treatment. The maximum flowrate was 20 IGPM. The overall treatment consisted of the following stages:

1. Coagulation, sedimentation and flotation; pretreatment reservoir of 9000 liter, sedimentation unit equipped with underflow and overflow weirs;
2. Filtration through two successive granular media filters;
3. Absorption through a special oleophilic media;
4. Adsorption through a series arrangement of activated carbon filters;
5. Phenol removal by chemical treatment.

4.1.3 RESULTS

The following table presents the average results of the water analyses showing the effectiveness of the water treatment process.

Table 3 CONCENTRATION IN PHENOLS, PAH's AND OIL AND GREASE; BEFORE AND AFTER GROUND WATER TREATMENT.

Parameter	Influent	Effluent
Total PAH (ppb)	2371	2.2
Benzo (a) pyrene (ppb)	11.6	0.05
Phenols (ppb)	187	5
Oil and grease (ppm)	58	6

Results courtesy of Canviro Consultants

4.2 CASE II

Restoration of an oily sludge lagoon in a shutdown petroleum refinery. Twelve hundred tons of oily sludge was transfered into a biolysis reactor for elimination of contaminants; the biosludge resulting from the process was used in part to help the cleanup of the lagoon area while the other part was dewatered for landfilling.

4.2.1 DESCRIPTION OF THE BIOLYSIS PROCESS

The biolysis process can be used on a large-scale basis to eliminate recalcitrant organic contaminants contained in a waste sludge. Simultaneously the process enables this waste to be detoxified.

As of now, over six thousand tons of oily sludges have been treated by this process for different projects; the average concentration levels of oil and greases falls from 15% to 2%. The results of the leachate tests conducted on detoxified sludges are in accordance with Quebec regulations and the finished product can therefore be considered as a non hazardous waste.

The biolysis process is a biological system which can be operated with a high concentration of solids. The organic contaminants which are non-soluble or difficult to biodegrade can be destroyed by this process.

The oily sludges must undergo a pretreatment to liquefy them prior to input to the system. They are then sent to a bioreactor in which the physico-chemical parameters as well as endocellular and exocellular microbial activity are controlled. The reaction is exothermic and a volume reduction of approximately 30% takes place. The process has been developped and is still being researched and upgraded by Sanexen engineers.

4.2.2 ELIMINATION OF PAH

Besides biodegrading oils and greases, the biolysis process works on the PAH. In the final phase of the process, the percentage of biodegraded material and the following concentrations are observed:

TABLE 6: EFFECTIVENESS OF THE PROCESS TO BIODEGRADE THE PAH

	PAH REDUCTION (list of 16, method 610 EPA)
$\frac{\text{Biodegraded mass}}{\text{Total mass input}}$	Biomass: 92% Biomass + bottom sludges: 85%

In the resulting biomass the biodegradation is excellent, that is over 90%. However, when bottom sludges to be reprocessed are taken into consideration, the overall effectiveness of the process decreases below 90%. Further reduction can be achieved through landfarming.

CONCLUSION

The restoration of sites contaminated with PAH's requires a good knowledge of the properties of the contaminants and it is important to know the components of the chemical mixture in order to design proper systems for the treatment of contaminated soils and groundwater. Site restoration methodology must still be determined on a case by case basis and site characterization remains of great importance.

In the case histories presented in this communication, the specific tools developped have showed good efficiency for the treatment of PAH's.

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CLEANUP FROM THE PESTICIDE WAREHOUSE FIRE -- CANNING, NOVA SCOTIA

R. Dutton and H. Whittaker
Environment Canada
Environmental Protection Service
Environmental Emergencies Technology Division

INTRODUCTION

On May 31, 1986 a fire occurred in the pesticide warehouse of Maple Leaf Farm Supplies in Canning, Nova Scotia. Many of the chemicals escaped as smoke and fumes, necessitating evacuation of the town. The local fire department doused the fire with in excess of 1,000,000 litres of water. Most of the runoff water escaped the site, flowing into a local farmer's pond and into the Habitant River by way of a culvert. Ground level vegetation and some trees along the pathway of the runoff water were killed. A substantial fish kill occurred.

A complete list of the 45 pesticides and herbicides stored in the warehouse is given in Table I. A total of 16 chemical compounds were found in various samples of runoff water and in samples from the warehouse floor; 8 of these compounds being found in significant concentrations. These 8 compounds are listed together with their LD_{50}(s)* in Table II.

Approximately 23,000 litres of the runoff water were contained in a hastily constructed trench surrounding the site. Subsequent rain diluted this water to 36,000 litres, which was then pumped into a tanker truck to await treatment. The solid remains of the warehouse and the surrounding area were coated with a mixture of the chemicals. The contaminated area was secured against public access.

On June 8, 1986 Sanivan of Sanexen of Montreal arrived at the site to commence cleanup operations. The EPS lab scale reverse osmosis (RO) unit was brought to the site to treat the contained runoff water.

PESTICIDE-CONTAMINATED SOLID TREATMENT

Sanivan was contracted by Maple Leaf Farm Supplies to cleanup the contaminated site and to arrange for disposal of contaminated rubble. On June 9, 1986 cleanup procedures commenced with the sorting of objects by size and relative degree of contamination.

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*A commonly used indicator of toxicity which is measured in ppm. The lower the ppm, the more toxic is the chemical.

TABLE I LIST OF PESTICIDES IN WAREHOUSE

PRODUCT	CONTAINER TYPE	AMOUNT
Agrox PSP 16%	10 kg Paper	640 kg
Agrox DL Plus	50 g Foil	9.75 kg
Amiben	22.7 kg Paper	22.7 kg
APM (Guthion)	2 kg Paper	248 kg
Atra Mix	10 L Plastic	480 L
Atrazine	10 L Plastic	1130 L
Banvel	10 L Plastic	70 L
Basudin	4L Metal	32 L
Benlate	2 kg Paper	12 kg
Bravo	10 L Plastic	720 L
Captan 50 WP	15 kg Paper	300 kg
Cymbush	500 g Paper	6 kg
Decis	1 L Metal	30 L
Dikar	15 kg Paper	450 kg
Dipel	500 g Paper	36 kg
Di-Syston 15G	20 kg Paper	100 kg
Dual 960 E	10 L Plastic	40 L
Easeout PSP	10 kg Paper	60 kg
Eptam 8E	20 L Metal	40 L
Equal	2 kg Paper	38 kg
Furadan 4.8	4 L Plastic	228 L
Gramoxone	5 L Plastic	115 L
Lannate	3.78 L Plastic	75.6 L
Lexone DF	2.5 kg Plastic	30 kg
Malathion 50 EC	10 L Plastic	80 L
Manzate	2 kg Paper	312 kg
Manzate	25 kg Paper	900 kg
MCPA	5 L Plastic	10 L
Monitor	10 L Metal	50 L
Patoran	10 L Plastic	130 L
Phygon	2 kg Paper	100 kg
Plictran 50 WP	1.5 kg Paper	10.5 kg
Polyram 80	10 kg Paper	1000 kg
Primextra	10 L Plastic	190 L
Ripcord	1 L Glass	6 L
Rival	9 L Plastic	54 L
Sutan 8E	10 L Plastic	500 L
Sutazine	10 L Plastic	80 L
System	10 L Plastic	40 L
Temik	15 kg Paper	615 kg
Terraklene	5 L Plastic	40 L
2-4-D 500	5 L Plastic	45 L
2-4-D 500	10 L Plastic	100 L
Vapam	18.9 L Plastic	1096.2 L
Vapam	113 L Plastic & Metal	904 L

TABLE II CHEMICAL COMPOUNDS DETECTED IN SIGNIFICANT LEVELS

COMPOUND	LD_{50}
Aldicarb (Temik)	0.9 ppm
Carbofuran	11 ppm
Methomyl (Lannate)	20 ppm
2,4-D Acid	370 ppm
Atrazine	1000 ppm
Dicamba Acid (Banvel)	2900 ppm
Sutan	4000 ppm
Dithiocarbamate Fungicides (Manzate)	>8000 ppm

Plastic pesticide containers and small objects from the floor of the warehouse were drummed for future disposal at a secure landfill. Drums were numbered and their contents recorded.

Large objects such as wood and corrugated metal roofing sections were scrubbed by hand using brooms and a one percent solution of Alkaquat DMB-451, an anionic heavy duty cleaner by Shur-Gain. The decontaminated objects were landfilled locally.

Over the course of the cleanup several rains washed the area and drained into the temporary trench surrounding the site. This contaminated rainwater was pumped to a tanker truck to await treatment.

On June 17, 1986 contaminant levels in a sample of recent rainwater taken from the trench were found to be low. Following this analysis collection of rainwater was halted and the trench was filled in.

On June 19, 1986 the concrete floor of the warehouse was swept clean. The 161 210-litre drums of contaminated solid material were stacked in the centre of the concrete floor to await shipment to a secure landfill. The Sanivan crew departed on June 20, 1986.

PESTICIDE-CONTAMINATED WATER TREATMENT

THE EPS LAB SCALE RO UNIT

The Environmental Emergencies Technology Division of EPS offerred the use of their lab scale reverse osmosis unit for treatment of the pesticide-contaminated water, as they wished to demonstrate the application of this technology to spill situations.

The EPS lab scale RO unit is a semi-self-contained vehicle-portable unit (Figure 1), an electricity source being its only external requirement. The reverse osmosis system consists of a feed pump, two 5 - 25 micron pre-filters, a high pressure pump, and a variable number of pressure vessels, each containing 1 or 2 membrane elements.

Operation of the unit is illustrated in Figure 2. The feed pump, once primed, feeds the solution to be concentrated or purified through the two pre-filters to the high pressure pump. The high pressure pump feeds the solution at a pressure of 50 - 1000 psi to the membrane(s). The flow through the membrane(s) is such that the concentrate from the first membrane becomes the feed for the second membrane, etc... The permeate is removed from each membrane and pooled. Valving allows a portion of the concentrate from the membrane bank to be fed back to the high pressure pump inlet where it is mixed with incoming feed. Recirculation valve adjustments allow varying ratios of permeate to concentrate flow rates to be achieved and maintained

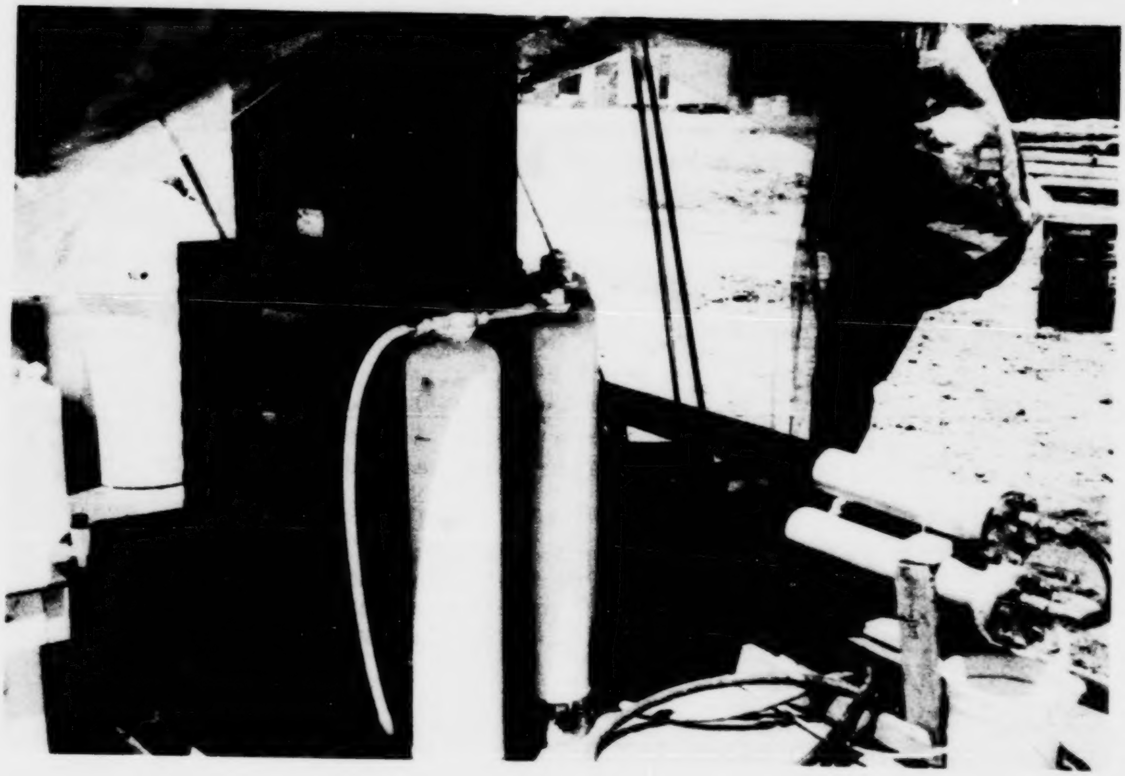


FIGURE 1

EPS LABORATORY SCALE RO UNIT
(EXTRA PRESSURE VESSELS & CARBON COLUMNS CONNECTED)

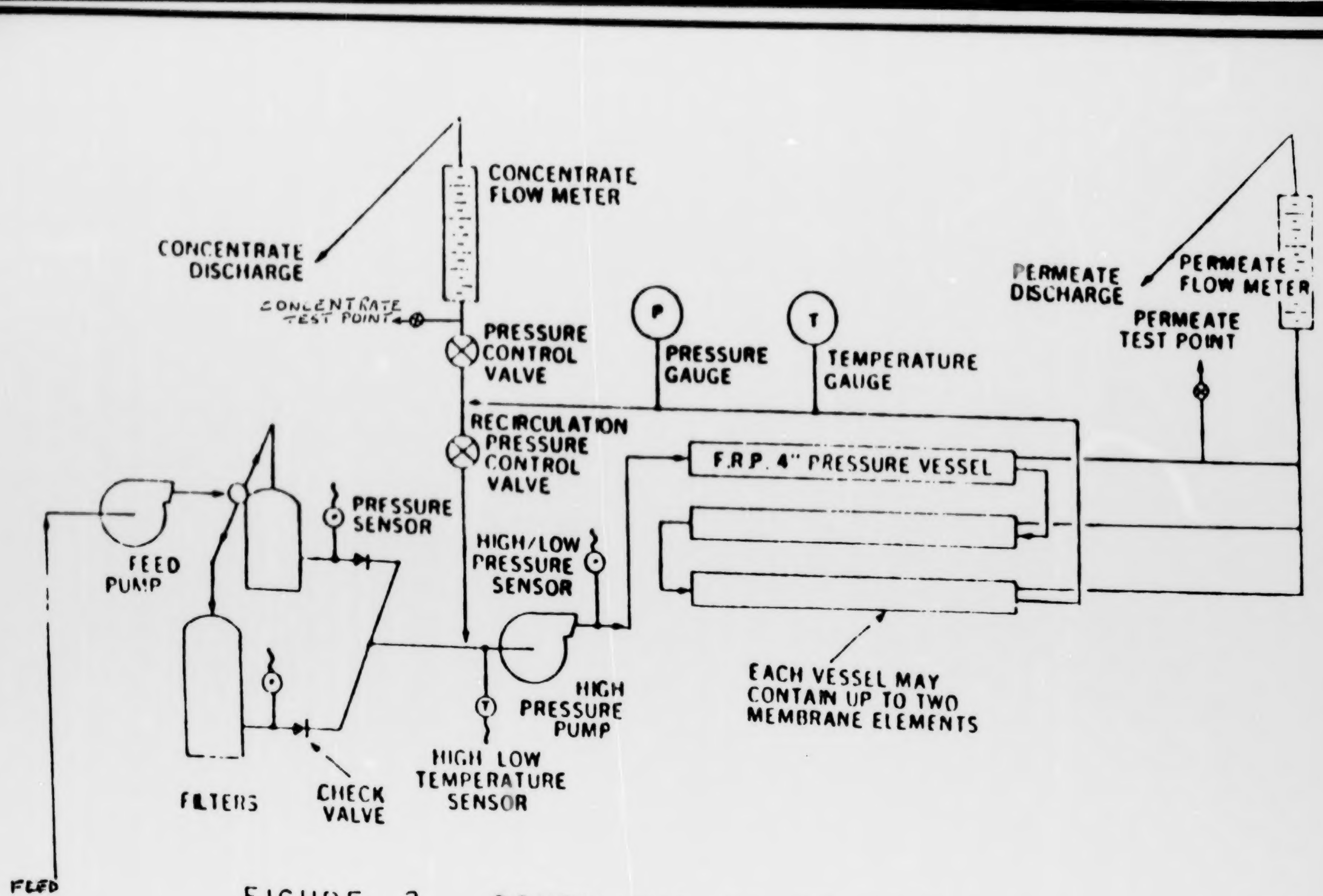

CONCENTRATE FLOW METER
CONCENTRATE DISCHARGE
CONCENTRATE TEST POINT
PRESSURE CONTROL VALVE
P
PRESSURE GAUGE
T
TEMPERATURE GAUGE
PERMEATE DISCHARGE
PERMEATE FLOW METER
PERMEATE TEST POINT
RECIRCULATION PRESSURE CONTROL VALVE
F.R.P. 4" PRESSURE VESSEL
FEED PUMP
PRESSURE SENSOR
HIGH/LOW PRESSURE SENSOR
HIGH PRESSURE PUMP
T
EACH VESSEL MAY CONTAIN UP TO TWO MEMBRANE ELEMENTS
HIGH LOW TEMPERATURE SENSOR
FILTERS
CHECK VALVE
FEED

FIGURE 2 SCHEMATIC OF RO UNIT OPERATION

(concentration ratio). Permeate and concentrate are then sent to either collection vessels or discharge as appropriate.

PROCEDURE AND RESULTS

On June 10, 1986 three of the six Toray membranes available at the start of the cleanup were installed in the unit and conditioned with dechlorinated tap water for 2 hours. A 1 hour salt-flux pre-test was then performed which established salt rejection capabilities at >99 percent. The unit was then shut down for the night.

Treatment of the pesticide-contaminated water began on June 11, 1986. The water contained in the tanker truck had a muddy appearance from particulates and metals picked up from the soil in the area. It was therefore pumped through a 5 micron bag filter and into a settling tank prior to feeding into the unit (Figure 3A). The concentrate from the RO unit was run through granulated activated carbon (GAC). The clear RO permeate and the GAC effluent were pumped to separate tanker trucks to await analysis prior to discharge. The unit was operated under these conditions for 9 hours. Fouling of the membranes then necessitated shutdown for cleaning, which consisted of a ½ hour dechlorinated tap water flush followed by a ½ hour citric acid (pH 2.5) flush. This cleaning procedure had little effect. It was therefore decided to flocculate the feed with 400 ppm of aluminum sulfate (Al_2SO_4) (Appendix A). The unit was then operated with the post-floc feed for 2 hours before cleaning and sutting down for the night (Figure 3B).

A bucket test demonstrated that ammonium hydroxide solution (pH 11) broke the floc and resuspended particulates. Acid wash (citric acid pH 2.5) solubilized metals and organics. On June 12, 1986 utilizing this information, a cleaning menu was established (Table III). The unit was then operated for 12 hours with 2 cleanings and then shutdown for the night with a sodium meta-bisulfite (SMB) soak.

TABLE III MEMBRANE CLEANING MENU

1. Flush with 50 litres of dechlorinated tap water.
2. Recirculate tap water for 30 minutes.
3. Recirculate ammonium hydroxide (pH 10.5-11) for 30 minutes.
4. Flush with 50 litres of dechlorinated tap water
5. Recirculate citric acid (pH 2.5-3) for 30 minutes.
6. Flush with 50 litres of dechlorinated tap water.

TABLE IV ANALYSES OF 4 MAJOR CONTAMINANTS (PPM)

Date & Time	COMPOUND	PRE FLOC FEED	POST FLOC FEED	FLOC PPT.	FIRST-PASS PERM.	% REJECTION	ONC.	GAC EFFLUENT	% ABSORPTION
11/6/86 11:00	Aldicarb	0.53	0.20	6.80	L0.001	> 99.50	5.90	L0.001	>99.98
	CARBOFURAN	2.30	0.12	22.00	0.0028	97.80	22.00	0.0028	99.99
	ATRAZINE	9.00	2.20	20.00	0.00057	99.98	INTF	0.0026	
	BUTYLATE	3.10	0.48	23.00	L0.001	> 99.79	3.90	L0.001	>99.97
11/6/86 14:30	ALDICARB		0.45		L0.001	> 99.78	3.90	L0.001	> 99.97
	CARBOFURAN		1.95		0.0019	99.90	17.00	L0.001	> 99.99
	ATRAZINE		0.51		0.0006	99.88	INTF	L0.001	
	BUTYLATE		2.00				7.9	L0.001	> 99.99
12/6/86 10:00	ALDICARB				0.0041		12.0	L0.001	99.99
	CARBOFURAN				0.0056		14.0	0.00062	99.99
	ATRAZINE				0.0230		45.0	0.0020	99.99
	BUTYLATE				0.0035		9.3	0.00061	99.99
13/6/86 10:00	ALDICARB		0.50		0.0012	99.76	15.0		
	CARBOFURAN		1.70		0.0043	99.75	18.0		
	ATRAZINE		0.820		0.0220	97.32	62.0		
	BUTYLATE		1.90		0.00039	99.98	9.60		
16/6/86	ALDICARB				0.0047			0.006	
	CARBOFURAN				0.0015			0.00082	
	ATRAZINE				0.0100			0.0037	
	BUTYLATE				0.0290			0.0400	

2 of 2

TABLE IV CONTINUED

Date & Time	COMPOUND	FLOC PPT.	POST FLOC FEED	FIRST PASS PERM.	SECOND PASS PERM.	% REJECTION	CONC.	GAC EFFLUENT	% AB-SORPTION
23/6/86 13:00	ALDICARB	1.30	1.20	0.0029		99.78	2.50		
	CARBOFURAN	20.00	28.00	0.0630		99.78	35.00		
	ATRAZINE	37.00	44.00	0.0330		99.93	69.00		
	BUTYLATE	8.5	12.00	0.0040		99.97	14.00		
25/6/86	ALDICARB			0.0110					
	CARBOFURAN			0.0270					
	ATRAZINE			0.0700					
	BUTYLATE			0.1360					
27/6/86 11:00	ALDICARB			L0.001	L0.001	-	0.47	0.26	SPENT
	CARBOFURAN			0.091	0.0021	97.69	1.40	1.50	
	ATRAZINE			0.140	0.0150	89.29	37.00	53.00	
	BUTYLATE			0.071	0.0046	93.52	12.00	15.00	
28/6/86	ALDICARB			0.025	L0.001	>96.00			
	CARBOFURAN			0.061	0.0022	96.39			
	ATRAZINE			0.051	0.0220	56.86			
	BUTYLATE			0.025	0.0018	92.80			

TABLE V METALS REMOVAL BY REVERSE OSMOSIS (PPM)

METAL	PRE FLOC FEED	POST FLOC FEED	PERM	% REJECTION	CONC.	GAC EFFLUENT
Mg	11.60	13.00	0.08	99.39	49.40	66.70
Ca	62.20	70.40	0.32	99.55	269.00	321.00
Fe (TOT)	2.33	1.15	0.05	95.65	2.33	7.18
Mn (TOT)	5.67	6.47	0.04	99.38	24.20	28.20
Ql (TOT)	1.16	7.12	0.05	99.30	6.47	4.38

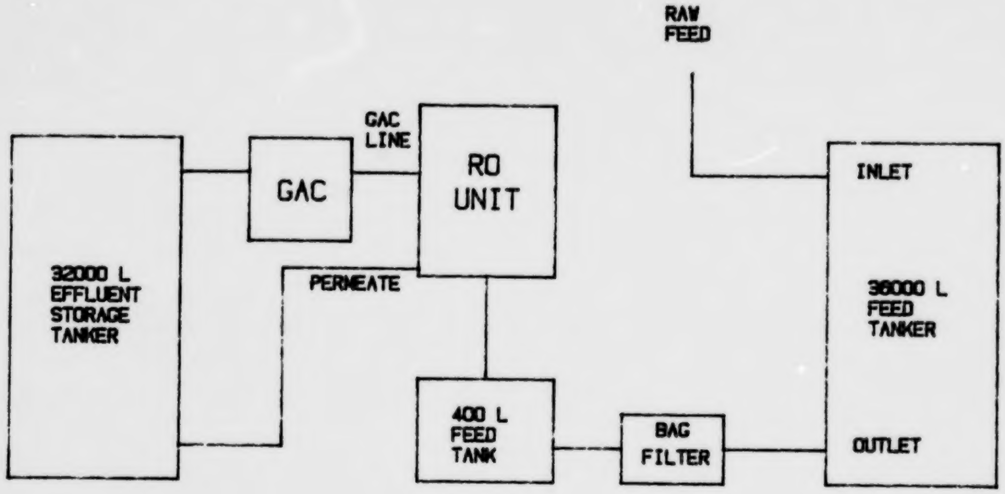

RAW
FEED
GAC
LINE
RO
UNIT
GAC
INLET
32000 L
EFFLUENT
STORAGE
TANKER
PERMEATE
36000 L
FEED
TANKER
400 L
FEED
TANK
BAG
FILTER
OUTLET

FIGURE 3A. FLOW DIAGRAM FOR CONTAMINATED WATER CLEAN-UP ON DAY ONE.

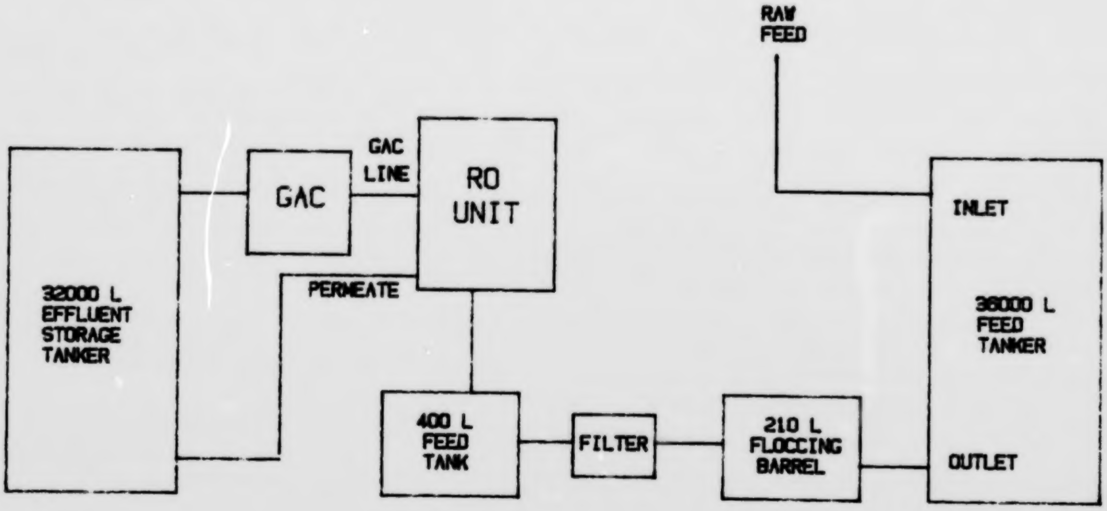

RAW
FEED
GAC
LINE
RO
UNIT
GAC
INLET
32000 L
EFFLUENT
STORAGE
TANKER
PERMEATE
36000 L
FEED
TANKER
400 L
FEED
TANK
FILTER
210 L
FLOCCING
BARREL
OUTLET

FIGURE 3B. FLOW DIAGRAM FOR CONTAMINATED WATER CLEAN-UP WITH IN-LINE FLOCCULATION.

Commencing on the morning of June 13, 1986 the unit was run continuously with 2 hour shutdowns for cleaning and intermittent 2 - 3 hour SMB soaks. The cleaning regime was dictated by the permeate flow rate which decayed slowly over 6 - 8 hour periods from 8 LPM to 4 LPM.

On the fourth day of operation (June 13, 1986) it became apparent that the bag filters used to remove the flocculatant from the feed were highly inefficient, breaking up the flocculatant and becoming clogged within a 1 to 2 hour period. The bag filter was therefore replaced with a fibre filter under low pressure. This easily removed the fluffy flocculatant.

On the fifth day of operation (June 14, 1986), two additional Toray membranes were added in series to bring the total number to 5 membranes on-line. This enabled the unit to run consistently at concentration ratios of 8:1 to 12:1 (Figure 4).

On June 17, 1986 (day 8) the 32,000 litre permeate tanker truck reached capacity at 0830. Following analysis of the permeate, which established all pesticide contaminants to be below background levels, it was discharged down a manhole and via a culvert into the Habitant River.

On day 13 (June 22, 1986) batch re-processing of GAC effluent was commenced and interspersed with the pesticide-contaminated water first-pass treatment. In conjunction with the re-processing operation, the high temperature alarm initiated shut-off of the unit on three separate occasions.

Processing of the feed and re-processing of the GAC effluent continued over days 14 - 17 and was completed on the morning of June 26, 1986. The concentrate was re-concentrated continuously during the afternoon and evening of June 26, 1986 until only eight 210 litre drums of super-concentrate remained. The unit was then cleaned and shutdown for the night with an SMB soak.

Analysis of the second batch of first-pass permeate found all contaminants to be present at slightly above background levels. Approximately 36,000 litres of first-pass permeate were therefore retreated on June 27 to June 28, 1986.

On June 29, 1986 (day 20) the resulting second-pass permeate was discharged while the resulting concentrate was re-concentrated continuously until only two 210 litre drums remained.

The 10 drums of superconcentrate were sealed for landfilling, together with 2 drums of flocculatant, 1 drum of contaminated solid wastes, 5 drums of sludge from the bottom of the contaminated water tanker and 2 drums of spent carbon. These drums were numbered 162 through 181 and stacked together with the 161 drums of contaminated solid material to await shipment to a secure landfill.

Final shutdown of the unit occurred at noon on June 29, 1986. Following shutdown, the membranes were cleaned and then transferred to a solution of SMB for transportation home. The ESP lab scale RO unit left the pesticide warehouse site at 1630 on June 29, 1986

DISCUSSION

The solid phase of the cleanup was accomplished quickly and safely using an established routine.

The heavy duty cleaner used in the decontamination of large solid objects was chosen on the basis of its anionic chemical make-up -- an anionic soap will not undermine the integrity of the membrane elements used in the reverse osmosis phase of the cleanup.

The Toray membranes used in the water phase of the cleanup were designed for the production of fresh water from salt water. Previous RO trials by EPS established good performance by Toray membranes in the treatment of pesticide and herbicide contaminated waters (1). Pretreatment (conditioning) is normally required to ensure long life and continuous high permeation rates.

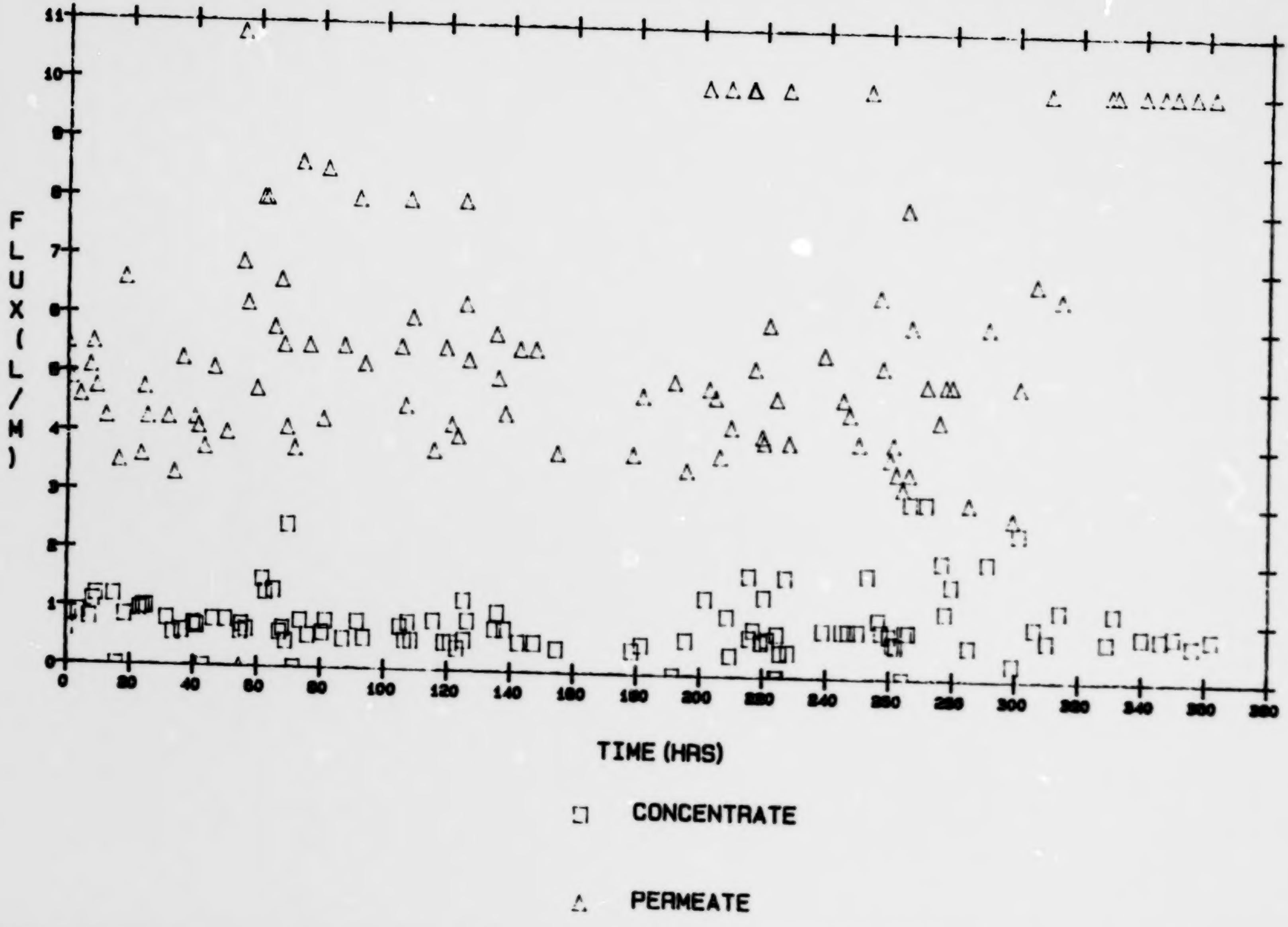
The RO unit was run on non-flocculated feed for 9 hours at the start of the cleanup. During this time flux rates decayed rapidly. Given the very turbid nature of the feed, this rapid decay is not surprising and can be attributed to particulate fouling of the membranes. However, despite the use of flocculated feed throughout the remainder of the first-pass portion of the treatment, subsequent cleanings did not yield significant flux rate recoveries. It is thus considered that excessive fouling experienced during the initial 9 hours of operation interferred with flux rates throughout the first part of the trial. Moreover, floccing did not remove all of the particulates so that fouling on a lesser scale continued throughout the cleanup.

During the production of second-pass permeate the flux rates fully recovered (Figure 4), indicating that continuous operation with the particulate-free first-pass permeate used as feed was sufficient to flush the fouled membranes. Rejection rates remained high (>90%) despite the low concentrations of the feed (first-pass permeate) during this latter part of the cleanup, indicating that the Toray membranes were fully recovered and had suffered no permanent damage through fouling from the turbid feed.

Pesticides stratified in the tanker truck such that the feed was more concentrated in the bottom layer of the tank. Feed was drawn from the surface of the tank. This explains why the first-pass permeate was suitable for disposal in the early part of the operation, while requiring retreatment in the latter

FIGURE 4

CANNING FLUX RATES



part of the operation. The concentration of the feed increased as the level of the feed tank diminished.

The flocculant removed some of the pesticides with the particulates (Table IV); the floc precipitate contained levels in the ppm range for all four major pesticides present in the contaminated water (Table IV). This fluffy, wet precipitate was drummed for landfill. Compression of the precipitate to reduce volume and fluidity of the material to be lanfilled would be highly desirable.

In the early stages of the operation, the combination of RO and GAC proved extremely effective (Table IV). In the latter part of the cleanup the supply of carbon ran out. Thereafter the concentrate was reconcentrated several times to reduce the volume as no more carbon was readily available. The super-concentrate was drummed for landfill. It would be more desirable to landfill solid spent carbon than liquid super-concentrate.

Sludge from the bottom of the contaminated water tanker filled 5 210-litre drums for landfilling. It would be desirable to reduce the liquid content of the sludge prior to drumming for landfill.

The contaminated water phase of the cleanup stretched out over 20 days. This length of time could be reduced in several ways. For example, more emphasis should be placed on feed pre-treatment. If a flocculant had been employed from the start of the cleanup excessive fouling would not have been experienced. Hence flux rates would have been higher throughout the treatment and the overall length of the cleanup would have been reduced. Stirring of the feed tank to prevent stratification of the feed may have eliminated the necessity to retreat 36,000 litres of permeate. An adequate supply of granulated activated carbon may have eliminated the necessity to retreat GAC effluent. etc...

CONCLUSIONS

The use of RO technology for emergency cleanup of contained contaminated water was proved to be an effective and suitable methodology. The use of RO technology to treat contaminated water enables contaminated solid structures to be washed on site and thus landfilled locally as opposed to removal to a secure landfill.

The combination of flocculation with RO-GAC allows the use of RO on even very turbid, muddy spill waters and reduces the contaminated substance to a small amount of solid spent carbon for disposal.

Methods for filtering flocculated feed and for compressing floc precipitate need to be developed. A method for compressing/centrifuging residual feed sludge on site needs to be developed.

Greater emphasis should be placed on pre-treatment of feed in order to facilitate quick and effective treatment by reverse osmosis.

An adequate supply of carbon should be brought to spill sites in order to reduce all contaminated waste waters to the solid spent carbon state.

ACKNOWLEDGEMENTS

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d. Mr. Jim Imrie, Miss Diane Radnoff and Mr. Michael Dutton for operation of the RO unit.

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APPENDIX A: TESTS FOR OPTIMAL Al_2SO_4 DOSE

Mixed stock solution of 1 ppt Al_2SO_4. Dosed 1 litre of feed with 200-550 ppm Al_2SO_4 in 50 ppm intervals. Optimal floccing occurred at 400 ppm.

Flocculant works best at pH 5.5. Addition of the flocculant lowers the pH to approx. 4.5. The pH of the feed varied in conjunction with layering of the pesticides. Where the feed pH was high (approx. 9.0) HCl was added to lower the pH to approximately 5.5 prior to floccing.

DEVELOPMENT AND DEMONSTRATION OF A MOBILE REVERSE OSMOSIS/ ADSORPTION TREATMENT SYSTEM FOR ENVIRONMENTAL CLEAN-UPS

H. Donison, ZENON Environmental Inc., H. Whittaker, J. Tremblay,
R. Dutton, Environment Canada

ABSTRACT

A system for treatment of organically contaminated waters resulting from chemical spills or landfill leachates was developed and demonstrated. The treatment system consists of two primary unit operations. The organically contaminated water is processed by reverse osmosis to produce a clean stream for discharge and a stream for further processing in which the organic contaminants have been concentrated up to ten times the original concentration. The concentrated stream suitable for discharge. The ultimate result of treatment is that the contaminated water can be treated on-site to produce a dischargeable effluent and the organic contaminants can be removed from the site adsorbed on a relatively small amount of carbon for incineration or disposal at a secure landfill.

The system was demonstrated for 60 days at two contaminated sites. At one site the system was used to treat water drained from areas where petroleum products had been spilled over a number of years. At the second site, leachate from a hazardous waste landfill containing a number of chlorinated and nonchlorinated solvents was treated. The results of the demonstrations showed that between 50 and 95 percent removal can be achieved for organic contaminants present in the feed at low ppm levels or less by this treatment system.

INTRODUCTION

Today's society uses large quantities of organic chemicals and organic chemical products. The production, transportation, utilization, and disposal of these organic chemicals often result in the accidental or unforseen release of these chemicals to the environment. This study is concerned with the remediation of contaminated water resulting from the release of organic chemicals. Of particular concern is the cleanup of water contaminated by accidental spill of chemicals or petroleum products and the cleanup of water contaminated by organic chemicals disposed of in inadequately sealed or improperly designed landfills.

To date, very limited work has been done on the development of clean-up technologies suitable for spill cleanup. Technologies for the emergency clean-up of contaminated ground or surface waters must meet the following criteria in order to respond to spills in potentially remote or undeveloped areas.

i) fully portable
ii) simple to assemble and to start up
iii) low utility requirements
iv) low maintainance requirements

Recent studies by the Environmental Protection Service, Environment Canada have demonstrated the utility of reverse osmosis (RO) as a method of concentrating dilute organic solutions resulting from chemical spills (Whittaker et al. 1985, Straforelli and Whittaker, 1985). A mobile, self-contained RO unit has been used by the EPS branch of Environment Canada to develop and demonstrate this technology for chemical spill clean-up. In field tests of the mobile unit, RO was demonstrated to be a technically and economically effective method of cleaning up spilled chlorophenate solutions and of treating dilute chemical landfill leachate.

A major drawback to RO treatment of chemical spills and landfill leachates is that it is not a final treatment method. Even at concentration factors as high as 10:1, 10% of the treated water (ie. the concentrate stream) cannot be discharged and must be further processed. This would often involve transporting large volumes of concentrated toxic solutions long distances to suitable liquid waste handling facilities.

Depending on the location of the chemical spill or landfill, the transportation costs could be considerable. Furthermore, in many locations it is desirable to reinject as close to 100% of the decontaminated water as possible to maintain the groundwater level or to facilitate contaminant containment strategies.

In order to reduce the cost of transportation and recover close to 100% of the contaminated water secondary treatment of the RO concentrate stream is required on-site. Adsorption is a well developed technology for removal of a wide variety of dissolved organic and inorganic contaminants from aqueous solutions and is suitable for treatment of the RO concentrate stream.

This paper describes the results of a study undertaken to develop and demonstrate a reverse osmosis system utilizing adsorption to treat the concentrate stream.

REVERSE OSMOSIS ADSORPTION SYSTEM

A schematic of the fundamental system configuration is shown in Figure 1.

Reverse Osmosis

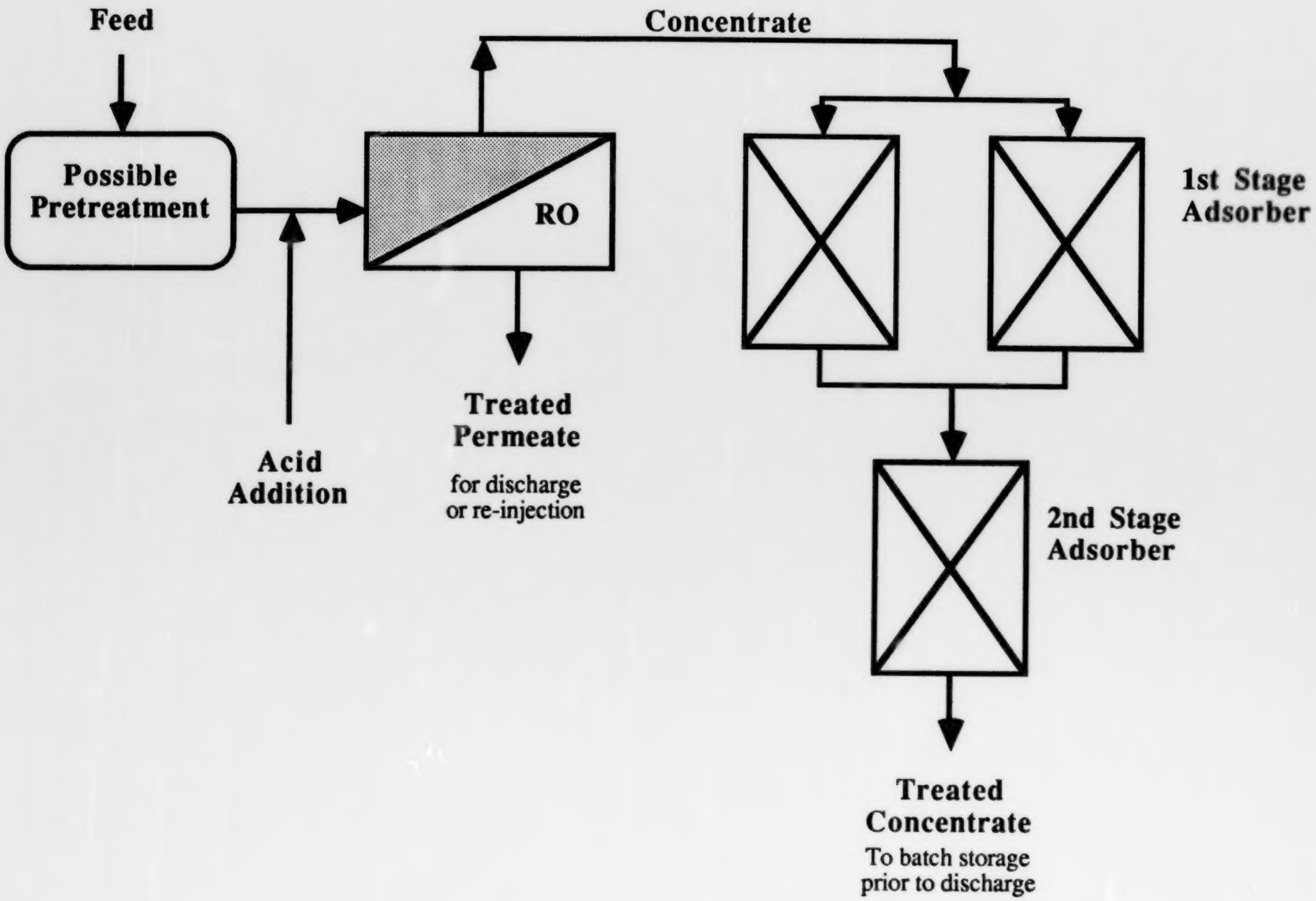
At the heart of the system is the reverse osmosis treatment unit. In this treatment unit the contaminated water is passed under pressures up to 1000 psi across a membrane surface. At the membrane surface, pure water preferentially permeates the membrane, leaving the suspended and dissolved contaminants concentrated on the feed side.

The amount of material removed (rejected) by the membrane is dependent on the type of reverse osmosis membrane used and the types of dissolved materials present. Rejection levels are dependent on the size and charge of the dissolved molecule with larger molecules and higher charge being more highly rejected.

Membrane filtration processes, like reverse osmosis, differ from traditional filtration as they have three flow streams while traditional filtration has two flow streams. Traditional filtration is referred to as dead-end filtration as feed flow is directly through the filter and all the material that is to be removed accumulates on the filter surface eventually resulting in plugging. Reverse osmosis is referred to as a cross-flow filtration process as the flow of feed is across the membrane surface. Cross-flow filtration has the advantage that the substance to be removed is concentrated in a third stream which is removed from the filtration module, thereby minimizing accumulation of the substance on the filter surface.

FIGURE 1

SCHEMATIC OF PROPOSED RO/ADSORPTION SYSTEM


Feed
Concentrate
Possible Pretreatment
RO
1st Stage Adsorber
Acid Addition
Treated Permeate
for discharge or re-injection
2nd Stage Adsorber
Treated Concentrate
To batch storage prior to discharge

The concept of reverse osmosis is illustrated in Figure 2. As Part A of Figure 2 illustrates, if a more concentrated salt (or other dissolved material) in water solution is placed across a semi-permeable membrane from a less concentrated salt solution, the natural process of osmosis will occur. That is, the membrane will permeate water from the less concentrated solution into the more concentrated solution until an equilibrium is established. The difference in head or pressure that is created across the membrane at equilibrium, as illustrated in Figure 2B, is known as the osmotic pressure of the solution.

If it is desirable to remove water from the more concentrated solution, pressure must be applied to the more concentrated solution as illustrated in Figure 2C. In order to have permeation of water from the more concentrated solution to the less concentrated solution (in effect reversing osmotic flow) the amount of pressure applied must be greater than the osmotic pressure.

The amount of pressure required to produce a reverse osmosis effect is dependent on the concentration of the original solution and the amount of water that must ultimately be removed. The more concentrated the starting solution and the higher the concentration factor desired, the higher the pressure that must be applied so that reverse osmosis will occur. Typical operating pressures range between 200 to 1000 psi.

The basic components of a reverse osmosis system are illustrated in Figure 3. As can be seen, the system is very simple, consisting primarily of a prefilter, a process pump, a reverse osmosis membrane module, and flow/pressure control valves. As a result of their simplicity of design, reverse osmosis systems are inherently easy to operate and maintain.

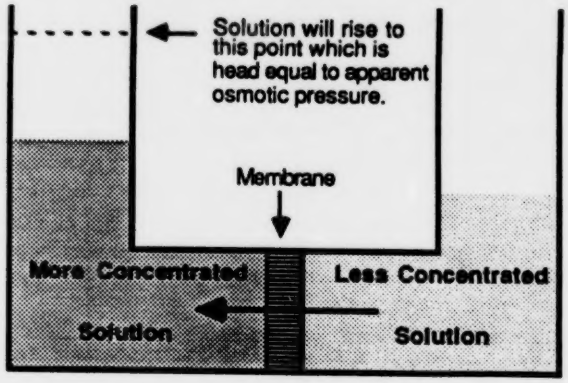
The concentration factor (ratio of the permeate flow rate to concentrate flow rate) can be controlled by controlling the rate at which concentrate is recirculated. The concentration factor may be limited by the osmotic pressure or, as is more frequently the case in natural water systems, by the precipitation of inorganic salts at the membrane surface. Inorganic salts precipitate when anions and cations have been concentrated past their solubility limit. This problem can often be minimized by adjusting the pH of the feed to increase the solubility of some of the more commonly precipitating salts.

Reverse osmosis membranes can be packaged in several ways. The basic configurations commercially available are tubular, capillary, spiral, plate and frame, and hollow fibre. For use in spill cleanup, it is desirable to maximize the amount of membrane area per unit volume of system so that the system is easy to transport. Each of the configurations listed has a different packing density with tubular systems having the least dense packing and hollow-fibre systems having the most dense packing. Unfortunately, a higher packing density will increase the level of pretreatment required for the feedstream; that is, the higher the packing density the greater the removal of suspended material required in pretreatment.

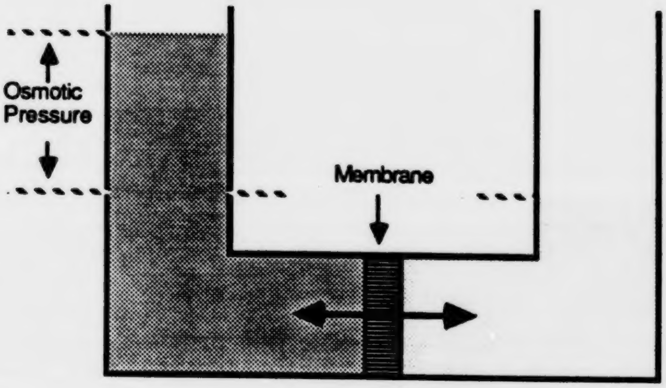
Carbon Adsorption

The other important unit process in this system is the granular activated carbon adsorption unit which is used to remove contaminants from the concentrate so that close to 100% of the treated water can be discharged on site. Activated carbon adsorption is widely accepted as a most effective and dependable technology for removal of the broad spectrum of dissolved organic impurities found in waters and wastewaters.

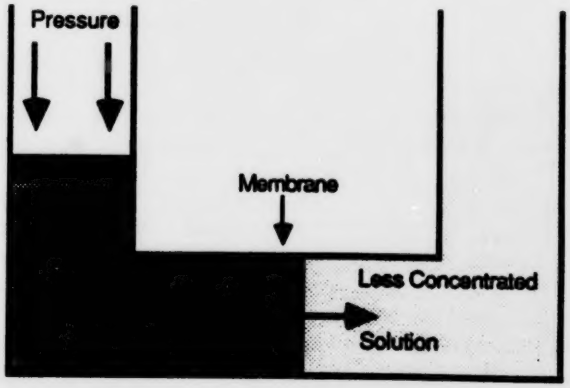
FIGURE 2 Concept of Reverse Osmosis


Solution will rise to this point which is head equal to apparent osmotic pressure.
Membrane
More Concentrated Solution
Less Concentrated Solution

A) Osmosis

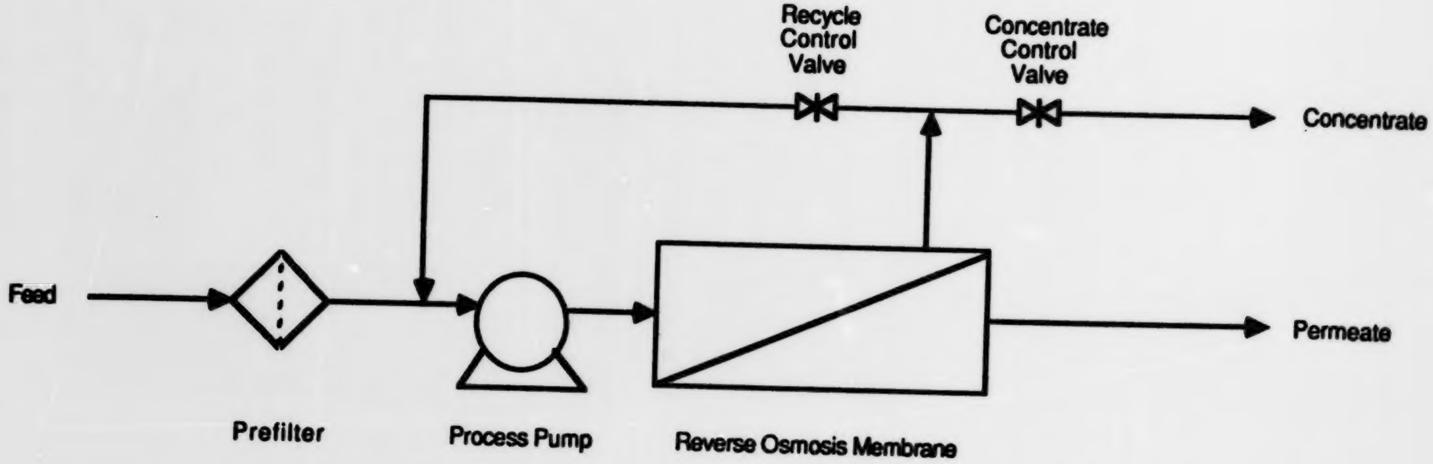

Osmotic Pressure
Membrane

B) Equilibrium


Pressure
Membrane
Less Concentrated Solution

C) Reverse Osmosis

FIGURE 3


Recycle Control Valve
Concentrate Control Valve
Feed
Concentrate
Permeate
Prefilter
Process Pump
Reverse Osmosis Membrane

Basic Reverse Osmosis System Flow Schematic

In the past 20 years, a considerable amount of research has been conducted concerning the removal of pure compounds from solution using granular activated carbon (GAC). Adsorption isotherms and kinetics performed in the laboratory are primary tools that have been developed to describe how specific organic chemicals can be removed in full-scale GAC applications.

Adsorption isotherms are plots of the equilibrium relationship between the amount of organic compound that is left in solution (equilibrium concentration, Ce) and the amount of compound that is on the surface of the activated carbon (surface concentration, q). Through the use of the isotherm plot, the relative adsorptive capacity of a given type of carbon can be estimated for specific compounds at different feed concentrations. Figure 4 plots a number of isotherms for pure, neutral compounds over seven orders of magnitude (McGuire and Suffet, 1980). The shaded area in Figure 4 depicts a general isotherm. At relatively high concentrations, the slope of the isotherm is relatively flat. As the equilibrium concentration decreases, the slope increases until it becomes equal to 1.0 (Radke and Prausnitz, 1972). In a GAC column the surface concentration or capacity, q, upon exhaustion of the carbon is in equilibrium with the feed concentration. In general as shown by the general adsorption isotherm in Figure 4 at concentration less than 10^{-5} moles/L (low ppm) a ten-fold increase in concentration of the feed would result in a ten-fold increase in the capacity of the carbon. The effect of this is that if the contaminant was concentrated ten-fold by reverse osmosis the amount of carbon necessary to recover the contaminant would be 10 times less than carbon adsorption technology alone.

The other major advantage of using reverse osmosis for concentration prior to adsorption treatment is that much smaller and more portable carbon columns can be used to treat the much lower flows.

The equilibrium capacity of activated carbon is dependent on the nature of the specific organic compounds adsorbed. An examination of adsorptivity generally reveals four clear trends.

i) Both organic and inorganic compounds can be adsorbed by activated carbon. Usually inorganic adsorption is relatively poor, however, studies have shown that activated carbon is an excellent adsorbent for heavy metal ions, particularly chromium and mercury.

ii) A decrease in solubility usually improves adsorption. Traube's rules states that the adsorption isotherms of homologous series compounds can be made to match each other by using reduced concentrations (actual concentration divided by solubility).

iii) Aromatic compounds generally adsorb better than aliphatic compounds with similar solubility.

vi) Functional groups such as hydroxyl, amino, and sulfonic acid decrease adsorption while halogens and nitro groups tend to increase it.

The effect of adsorbate molecular weight is somewhat clouded by pore size limitations. As molecular weight is increased, solubility usually decreases and, therefore, adsorption increases for relatively low molecular weight substances (Giusti et al, 1974). On the other hand, as molecular weight increases to the extent that some pores become unavailable, adsorption loadings may start to go down.

The rate of adsorption of a specific compound from solution will also influence the technical and economic feasibility of adsorption treatment for a particular application.

FIGURE 4

GENERAL AND SPECIFIC ADSORPTION ISOTHERMS
(from McGuire and Suffet 1980)

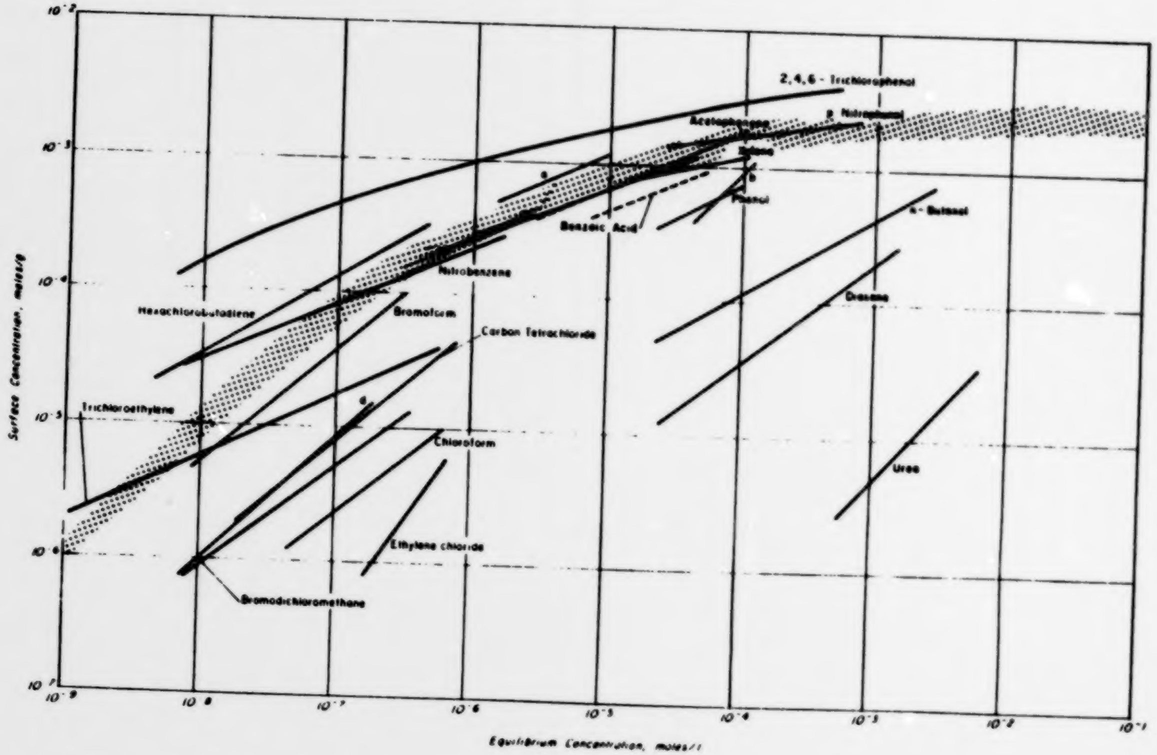


Figure 4. General and specific adsorption isotherms [35, 37, 38]. a - (di)-*n*-butyl phthalate; b - bis (2-chloroethyl) ether; c - dimethyl phthalate; d - dibromochloromethane.

In many spills the organic contaminant to be recovered will be dissolved in water containing relatively large concentrations of natural organics or in the case of leaking landfills, a complicated mixture of organic contaminants must be adsorbed. In general, the relative concentrations of competing species, their degree of competition (ie. stronger versus weaker adsorbing compounds) and their relative diffusive properties will influence the ultimate capacity of a carbon adsorber to adsorb a specific organic. Synthetic organics can be expected to compete with the natural organics which may be present at much higher concentrations. The competitive effect of the natural organics is difficult to predict theoretically as the nature and adsorptibility of the natural organics will be different for each water source. It is impossible to predict with accuracy the adsorption behaviour of a particular compound in a natural water matrix without laboratory isotherm and kinetics tests. However, many literature sources are available (eg. Dobbs and Cohen, 1980) which provide single solute isotherm for most common organic chemicals. This data can be used to provide an estimate of carbon adsorption effectiveness for a particular application.

SYSTEM DEVELOPMENT AND DEMONSTRATION

For the purposes of this project, the Environmental Emergencies Technology Division (EETD) of the Environmental Protection Service supplied their mobile reverse osmosis unit. This versatile unit has been used to demonstrate RO technology for the treatment of many environmental cleanups and industrial waste streams. A schematic diagram of this RO unit is shown in Figure 5. This system can contain up to 12 spiral wound membrane modules in six pressure vessels.

The other major unit, the granular activated carbon columns and their associated prefilter, was supplied by the Wastewater Technology Centre, Environment Canada. A schematic for this system is shown in Figure 6.

For development and demonstration of the RO/Adsorption system, two contaminated water sources were chosen for treatment. One source was the contaminated leachate from the Gloucester Landfill, a former chemical waste landfill and the other source was drainage water from a petroleum and petrochemical transfer station. For each source the contaminated water was chemically characterized and laboratory bench scale tests were undertaken to determine the most appropriate membrane type and adsorbent type for use in field demonstrations.

Case 1 - Gloucester Landfill

The Gloucester landfill site is a former municipal landfill which federal government labs in the Ottawa region used as a special waste compound for hazardous wastes from 1969 to 1980. The toxic organic contaminants disposed of there have begun to migrate toward local water well supplies via two aquifers. A wide variety of contaminants, including many chlorinated and aromatic organic solvents have been detected at this site.

The results of the initial raw water characterization are shown in Table 1. As shown, the water was significantly contaminated by volatile organic chemicals. These volatile organics include primarily chemicals used as laboratory solvents. The extractable organics were present at much lower concentrations than the volatiles and included a number of phthalate compounds together with a range of compounds likely resulting from degredation of

FIGURE 5 SCHEMATIC OF MOBILE REVERSE OSMOSIS TREATMENT UNIT

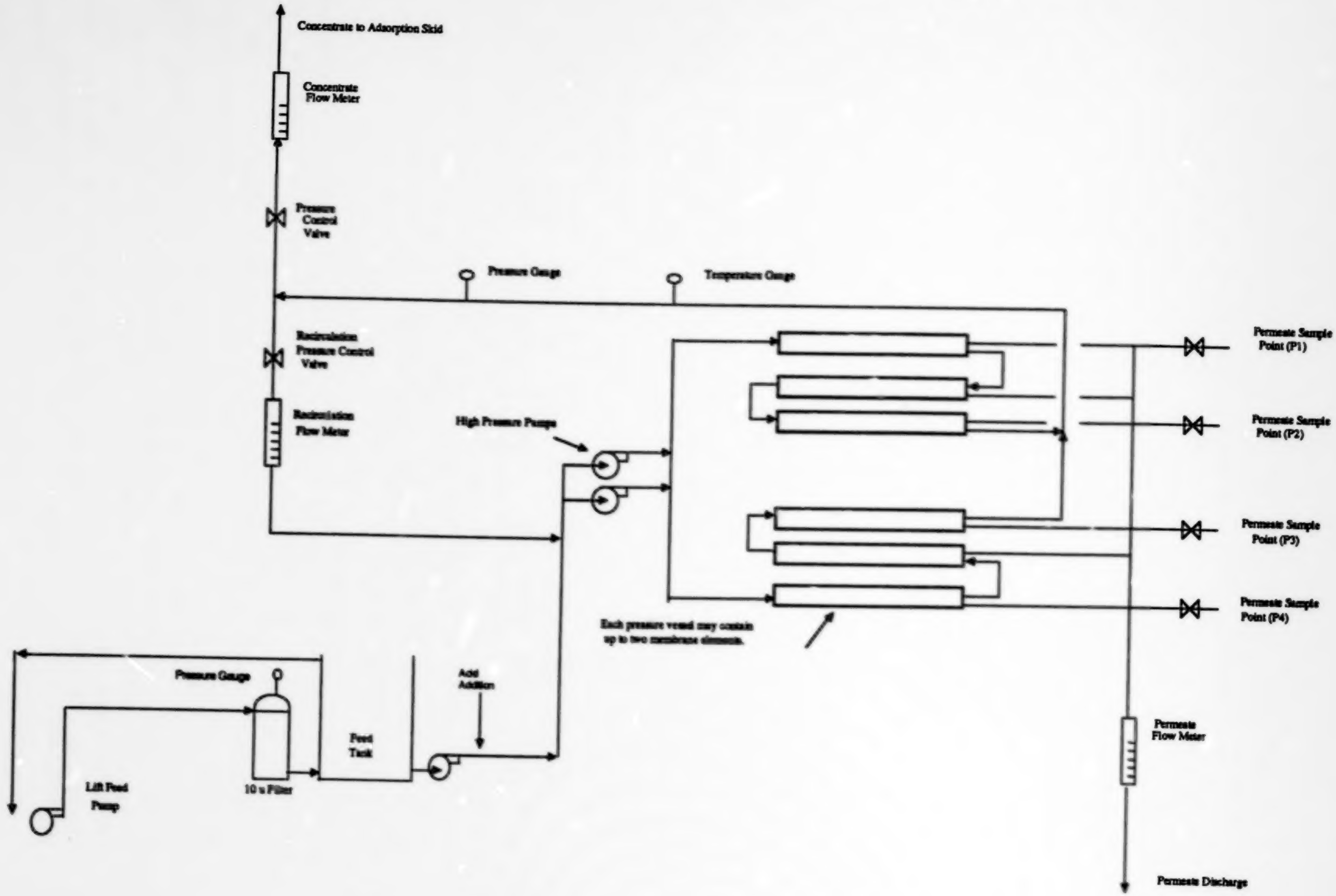

Concentrate to Adsorption Skid
Concentrate Flow Meter
Pressure Control Valve
Pressure Gauge
Temperature Gauge
Recirculation Pressure Control Valve
Recirculation Flow Meter
High Pressure Pumps
Permeate Sample Point (P1)
Permeate Sample Point (P2)
Permeate Sample Point (P3)
Permeate Sample Point (P4)
Each pressure vessel may contain up to two membrane elements.
Pressure Gauge
Acid Addition
Feed Tank
Lift Feed Pump
10 u Filter
Permeate Flow Meter
Permeate Discharge

FIGURE 6

ADSORPTION SYSTEM FLOW DIAGRAM

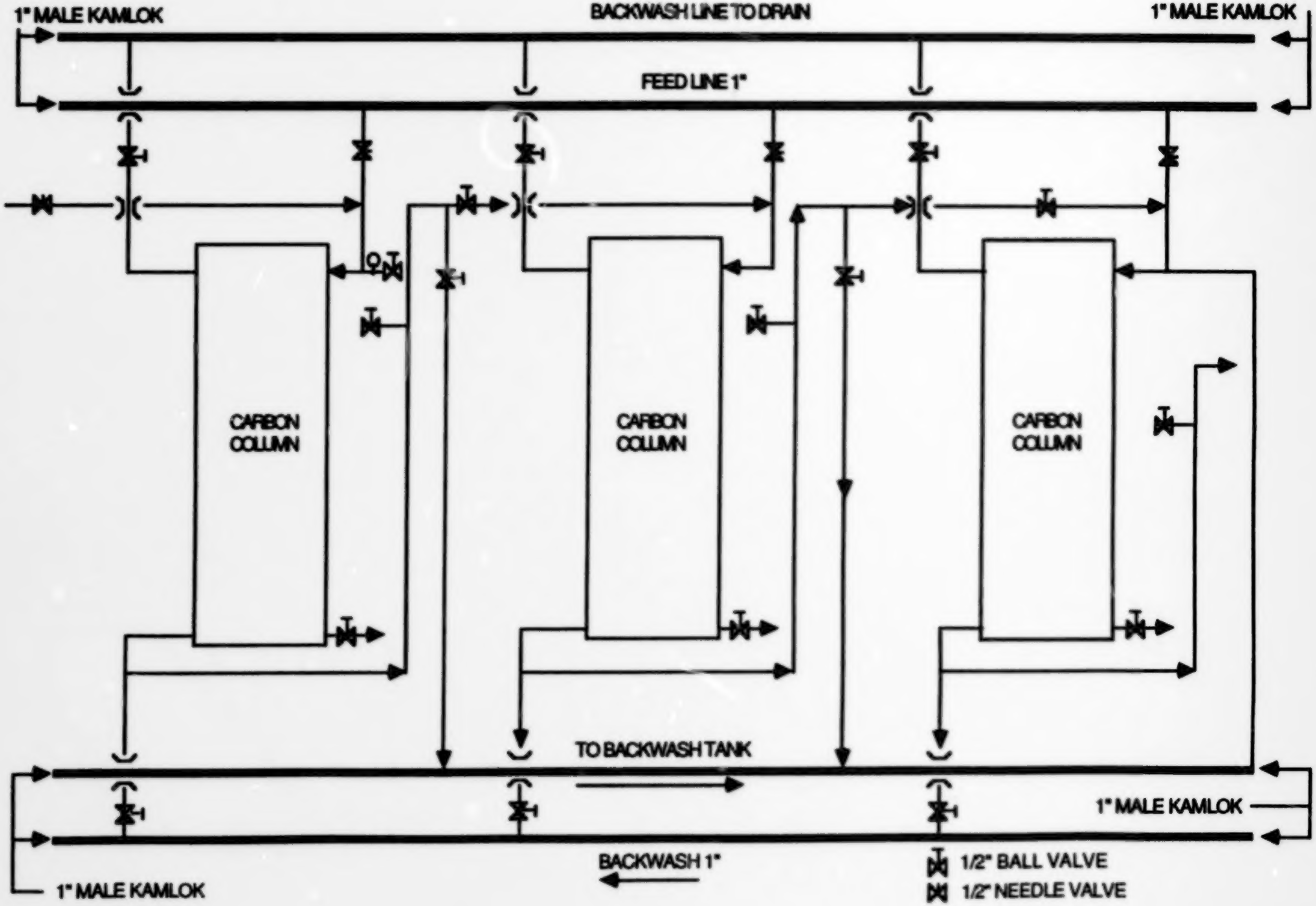

1" MALE KAMLOK
BACKWASH LINE TO DRAIN
1" MALE KAMLOK
FEED LINE 1"
CARBON COLUMN
CARBON COLUMN
CARBON COLUMN
TO BACKWASH TANK
1" MALE KAMLOK
BACKWASH 1"
1" MALE KAMLOK
1/2" BALL VALVE
1/2" NEEDLE VALVE

TABLE 1
INITIAL CHARACTERIZATION OF GLOUCESTER WATER

pH (20°C)	7.760
Conductivity (mmho)	0.622
TDS (mg/L)	740
TSS (mg/L)	19
Hardness (mg/L as $CaCO_3$)	330
TOC (mg/L)	18
Anions (mg/L)	
Fluoride	<0.01
Chloride	41
Nitrite as N	<0.02
Bromide	<0.08
Nitrate as N	<0.02
Phosphate as P	<0.08
Sulfate	46
Alkalinity	280
Metals (mg/L)	
Calcium	71
Magnesium	25
Sodium	14
Potassium	2.2
Aluminum	<0.03
Barium	0.19
Beryllium	<0.0003
Boron	0.23
Cadmium	<0.002
Chromium	<0.004
Cobalt	<0.01
Copper	<0.006
Iron	<0.01
Lead	<0.04
Manganese	<0.005
Molybdenum	<0.02
Nickel	<0.009
Phosphorous	<0.10
Silicon	3.3
Silver	<0.01
Strontium	0.2
Thallium	<0.02
Titanium	<0.01
Vanadium	<0.02
Zinc	<0.005
Zirconium	<0.01

TABLE 1 Continued

Volatile Organics (ug/L)	
1,1 Dichloroethane	351
1,2 Dichloroethane	NQ
Dichloromethane	194
1,1,1 Trichloroethane	124
Trichloroethylene	860
Toluene	270
Benzene	NQ
Chloroform	116
Diethylether	2767
Extractable Organics (ug/L)	
Phenol	1.3
Methyl phenol	2.5
Trimethyl cyclohexane	3.3
2-Nitrophenol	22
Methylbenzoic acid	5
Chloromethyl phenol	4.7
Dimethyl benzoic acid	1.4
Ethyl benzoic acid	1.2
Trimethyl benzoic acid	5.4
Dichloro benzoic acid	0.78
4-Nitrophenol	5.2
Dichloromethoxy benzoic acid	27
Chloromethoxy phenoxy propanoic acid	16
Di-n-butyl phthalate	10
Chlorophenyl triazine diamine	10
Bis-2-ethylhexyl phthalate	70
Di-n-octyl phthalate	1.9

NQ - identified but not quantified

natural and synthetic compounds. The organic compounds of concern for treatment are the volatile organics, thus for evaluation of treatment efficiency during the demonstration trial volatile organics were routinely monitored. This water is a good candidate for RO/Asdorption treatment as the suspended solids, iron, and silicon levels are relatively low. Based on equilibrium calculations, calcium salts would potentially precipitate upon concentration, however, theoretical equilibirum calculations prior to start up indicated that reducing the feed pH to approximately 6.5 would prevent calcium salt precipitation.

The membranes used for this demonstration were six Toray PEC 1000 4 x 40 spiral wound membranes in series and six Filmtec FT30 4 x 40 spiral wound membranes in a parallel series. The membranes were selected based on their ability to reject dissolved volatile organics in bench scale tests and in previous RO trials at the Gloucester landfill (Whittaker, 1985).

The carbon used in the adsorption columns was Calgon Filtrasorb 400 (F400). The carbon used was chosen based on isotherms derived in laboratory tests with samples of concentrated Gloucester water. The F400 carbon was selected from 6 adsorbents evaluated in laboratory testing. The 6 adsorbents included 3 activated carbons and 3 synthetic adsorbents. The 3 activated carbons were Calgon's F400, Norit ROW 0.8 Supra and AC Carbon CNS-200, an activated coconut shell carbon produced in Canada. The 3 synthetic adsorbents were Rohm & Haas Amberlite XAD-4, a synthetic polymeric adsorbent, Union Carbide Silicalite, a silicon based molecular seive and Imbiber beads, a cross linked polymer. In the limited laboratory tests performed, the activated carbons were observed to have much larger adsorption capacities for the volatile organics than the synthetic adsorbents. Between the activated carbons, significant differences were not observed in these limited tests. Filtrasorb 400 was chosen because of its ready availability and because of the large volume of published data concerning its use.

The field trial of the RO/Adsorption system at the Gloucester Landfill ran continuously from July 1 to August 28, 1986. Operationally, the trial was successful with a minimum of downtime for cleaning the membranes and general maintainance. The RO system was operated at a mean concentration factor of 8:1 (permeate flow:concentrate flow).

The most important parameters in judging the success of the system is the rate of processing and effectiveness of removal of contaminants.

Over the course of the trial the system was able to process an average of 30 L/min. The rate determining factor is the permeate rate across the membranes. Figure 7 shows the permeate rates for the Toray membranes and the Filmtec membranes for the entire trial. This figure shows that the permeate rate of the Filmtec membranes was initially 3 times greater than the Toray membranes but that over the duration of the trial the Filmtec permeate rate decreased to a rate less than the Toray membranes. The Toray membranes permeate rate was consistent throughout the trial.

Table 2 presents the mean concentrations for the duration of the trial of the volatile organics in the feed, concentrate, Toray permeate and Filmtec permeate streams, and the effluent from the GAC column. Table 2 also shows the percent rejections for the volatile organics for each membrane type. The Toray membrane performed significantly better than the Filmtec membrane for the rejection of all volatile organics monitored except chlorobenzene. The rejections were in general very good, with all compounds rejecting over 70% except for trichloroethene and chlorobenzene. Diethyl ether, 1,1,1-

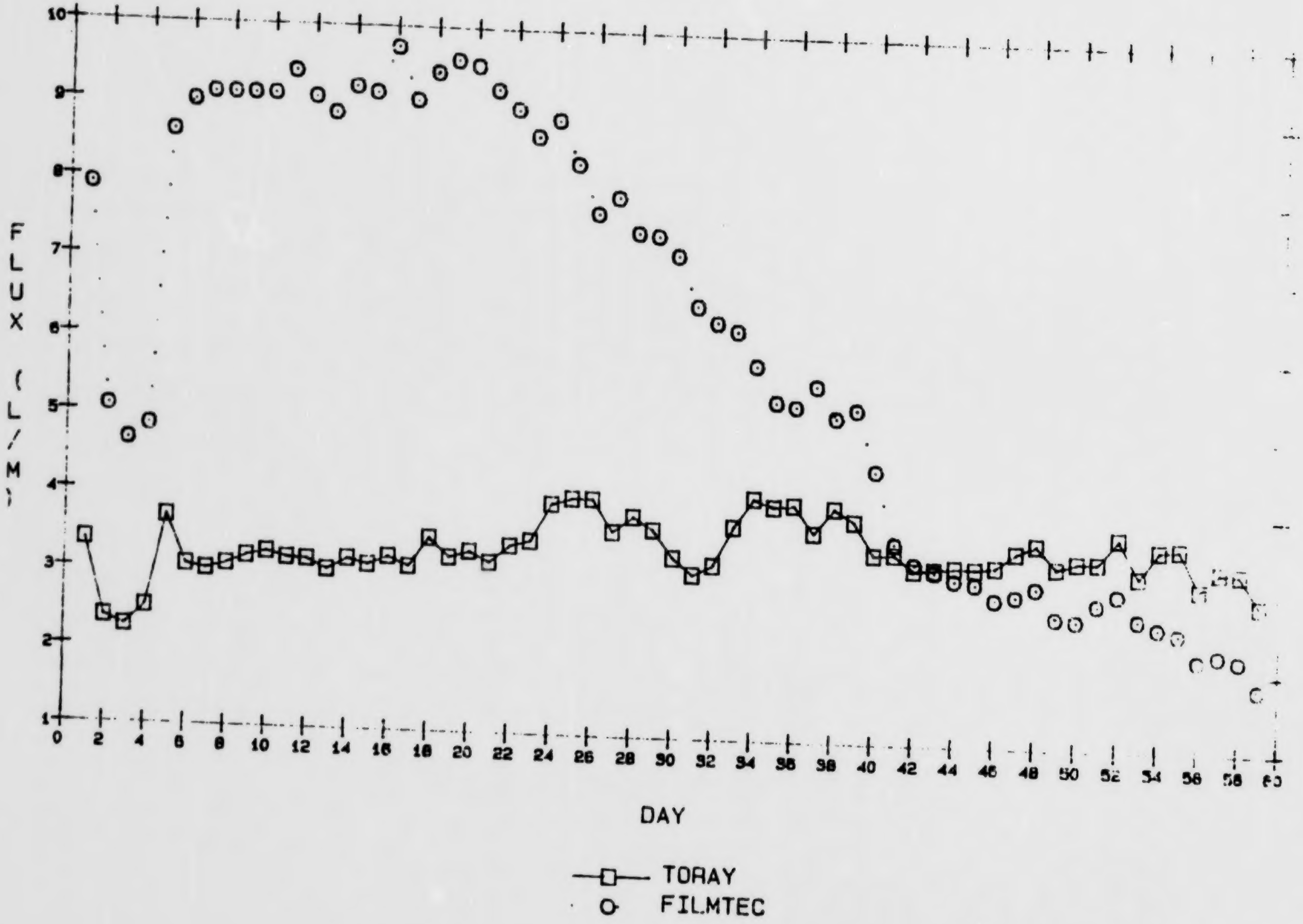
TABLE 2

MEAN VALUES BASED ON RAW DATA (PPB)
GLOUCESTER LANDFILL 1986 TEST OF RO/GAC SYSTEM

Chemical	Feed	Concentrate	Toray Permeate		Filmtec Permeate		Post GAC	
			Conc.	% Rejected	Conc.	% Rejected	Conc.	% Adsorbed
1,1 Dichloroethane	474.3	4018.8	52.1	89.0	90.5	80.9	884.9	78.0
1,1 Dichloroethene	11.3	64.4	3.3	70.8	5.2	54.0	12.7	80.3
Diethyl Ether	302.5	2343.2	20.7	93.2	33.5	89.0	666.9	71.5
Chloroform	369.5	2773.4	51.0	86.2	87.5	76.3	414.4	85.1
1,2 Dichloroethane	128.4	834.6	35.8	72.1	57.7	55.1	166.6	80.0
1,1,1 Trichloroethane	166.8	1282.4	3.3	98.0	9.0	94.6	43.1	96.6
Trichloroethene	455.4	2301.7	206.3	54.7	189.2	58.5	18.7	99.2
Benzene	1213.1	10543.0	101.3	91.6	219.8	81.9	191.2	98.2
Toluene	216.1	1769.5	15.0	93.1	34.8	83.9	4.4	99.8
Chlorobenzene	12.2	30.7	5.4	55.7	2.7	77.9	5.5	82.1

FIGURE 7

B6 GLF PERMEATE FLUXES



trichloroethane, benzene, and toluene were all rejected at greater than 90% by the Toray membrane.

The concentrate stream was fed to the GAC columns where the removal efficiencies were very good as shown in Table 2. The percent of the concentration adsorbed for each of the volatile organics monitored was greater then 70% and for the larger, less soluble compounds (1,1,1-trichloroethane, trichloroethene, benzene, toluene) the removal efficiency was greater than 95%.

The overall treatment efficiency of the RO/adsorption system as measured by the % removal of each of the volatile organics is shown in Table 3. The % removal was calculated based on the feed concentration and the blended effluent concentration was calculated assuming equivalent Toray and Filmtec permeate flowrates and a concentration ratio of 8:1, permeate to concentrate. The overall treatment efficiency ranged from a high of 94% removal of 1,1,1-trichloroethane to a low of 53% removal of 1,2-dichloroethane. The overall treatment efficiency would have been even greater if Toray PEC 1000 membranes had been used exclusively.

Case 2 - Drainage Water

The RO/adsorption system was demonstrated at a petroleum and petrochemical marketing and transfer site. The site has been in use for over fifty years and during that time, inevitably, petroleum and petroleum products were spilled in the tank farm area and parking and transfer areas. Water draining the tank farm is collected in a lagoon prior to discharge. The lagoon effluent combined with water draining a parking lot and loading area was treated with the RO/adsorption system for demonstration purposes.

Initial GC/MS characterization of the combined drainage waters showed ppb levels of the following volatile organics: benzene, ethylbenzene, toluene, and xylenes. Extractable organic contaminants detected by GC/MS analysis included primarily alkyl benzenes (C_2, C_3, C_4, C_5 and C_6) and aliphatic hydrocarbons. All organics identified were typical of petroleum or petroleum products. The total organic carbon (TOC) value was 30 mg/L which represents the identifiable extractable organics together with a large amount of non extractable or non identifiable organics which are likely degredation products of natural or petroleum products. The inorganic characterization revealed relatively high concentrations of sodium and chloride which may be a result of road salt contamination. As discussed earlier, the ionic concentration affects the pressure required to reverse osmosis but this is generally only significant at salinities greater than seawater. The inorganic characterization also showed high iron concentration (approx. 1.0 ppm). High iron concentrations are often encountered around industrial locations and often cause problems in RO treatment. At iron concentrations greater than 0.5 ppm iron will often deposit on the membrane surface and is not removed in routine cleaning procedures. If the iron concentration is not too great the problem can often be overcome by reducing the pH to help maintain the iron in the soluble form. The calcium levels were moderate and equilibrium calculations indicated that the feed pH should be reduced to 6.0 to prevent calcium carbonate precipitation.

The field testing of the RO/adsorption system at the petroleum site ran from April 18, 1986 to June 4, 1986.

The feed was filtered and the pH adjusted to between 5 and 7 to prevent calcium carbonate from depositing on the membranes. Initially the feed was fed to 2 banks of membranes in parallel. Each bank contained 6 membranes in

TABLE 3
RO/ADSORPTION SYSTEM TREATMENT EFFICIENCY FOR THE TREATMENT OF GLOUCESTER LANDFILL LEACHATE

Chemical	Feed (ppb)	Blended Effluent (ppb)	% Removal
1,1-Dichloroethane	474.3	161.7	66
1,1-Dichloroethene	11.3	5.2	54
Diethyl ether	302.5	98.2	68
Chloroform	369.5	107.6	71
1,2-Dichloroethane	128.4	60.1	53
1,1,1-Trichloroethane	166.8	10.2	94
Trichloroethene	455.4	177.9	61
Benzene	1213.0	164.0	86
Toluene	216.1	22.6	90
Chlorobenzene	12.2	4.2	65

series, one bank contained Filmtec membranes, the other contained Toray membranes. During the demonstraiton trials the configuration was changed a number of times in response to problems encountered. The unit was operated at 800 psi, with an optimum permeate flow rate of 8 U.S.gpm with 12 membranes and 6.7 U.S.gpm with 6 Toray membranes. The permeate to concentration ratio was approximately 4 to 1. The permeate from the RO unit was discharged or collected and stored in a tank for flushing and cleaning the membranes when required. The concentrate was sent to the adsorption unit.

The first two columns of the adsorption unit were in parallel and contained Calgon's Filtrasorb 400 carbon, one carbon column being on stand-by. The carbon columns were changed about every 8 days. The last column, in series with the carbon columns, contained Silicalite. The total amount of concentrate processed through the columns was about 76,400 L.

The major problem encountered during the field testing was fouling of the reverse osmosis membranes resulting in low permeate rates and short run times between cleaning. Another problem encountered was telescoping of both types of membranes. This was likely the result of excessive pressure on the inlet due to the fouling problems. These problems were dealt with by initiating different cleaning regiments, and making modifications to the filtering system and recirculation line.

The main foulant initially was iron hydroxide, a low pH wash using either citric acid or a dilute HCl solution was successful in cleaning the membranes, although run times between cleanings were very short. The major source of iron was the parking area drainage. Processing of this feed source was ceased and fouling problems were found to be less severe. Fouling continued to occur however and an autopsy on one of the membranes revealed an oily layer containing very small particles coating the membrane surface. A number of membrane cleaners were tested by placing pieces of the fouled membrane in beakers containing cleaning solutions. Hot alkaline detergent was found to be the most effective cleaner for removing the oily film. This cleaner was used on full scale and demonstrated to be very effective.

Originally, the filtering system consisted of a 25 u bag filter placed before the feed tank, then a 10 u Jacuzzi filter located within the mobile RO unit. Concentrate was recirculated back to the 10 u Jacuzzi filter. To reduce fouling, the recirculation line was placed before a more extensive filtering system consisting of a 25 u cartridge filter, a 10 u Jacuzzi filter, and a 5 u bag filter before being fed to the membranes.

Table 4 summarizes the average concentration of the organics monitored during the demonstration at Shell. The table shows the total organic content and the specific organics monitored were well rejected by both membranes. A general trend for increased rejection with increased molecular size is observed, as expected. Although good rejections were observed, the permeate flow rates were, in general, very low due to fouling as discussed above. During the first 15 days of the trial, the permeate rates for the Filmtec and for the Toray membranes were 0.74 and 0.78 liters per minute per membrane respectively.

The average organic concentrations for the effluent from the carbon adsorption and the silicalite column are also shown in Table 4. The removals of the specific organics by carbon were very good. Approximately two orders of magnitude for xylene, ehtylbenzene, and toluene and one order of magnitude for benzene and hexane. However, the effluent contained a significant non-adsorbable fraction of non specific organics as shown by the TOC results.

TABLE 4 AVERAGE ORGANIC CONTENT AT SPECIFIED SAMPLING POINTS

Parameter	Raw Feed (mg./L.)	Toray Permeate (mg./L.)	Filmtec Permeate (mg./L.)	Adsorption Feed (mg./L.)	Carbon Effluent (mg./L.)	Silicalite Effluent (mg./L.)	% Rejection Toray	% Rejection Filmtec
TOC	74.2	17.7	16	219.8	108.8	101.9	76%	78%
Ethylbenzene	0.23	0.03	0.13	0.54	0	0	87%	43%
Benzene	1.31	0.43	0.47	2.6	0.12	0.17	67%	64%
Xylenes	2.74	0.4	0.75	3.86	0.01	0.01	85%	73%
Toluene	0.09	0.02	0.03	0.19	0.01	0	78%	67%
Hexane	0.3	0.01	0	0.57	0.03	0.02	97%	100%

These non-adsorbable compounds are likely larger natural and oil type organics.

The Silicalite column was not successful in improving the effluent quality.

CONCLUSION

This study showed that reverse osmosis technology can be used to successfully treat water contaminated by toxic volatile organics and that granular activated carbon adsorption columns can be successfully used to remove the toxic volatile organics from the concentrate produced by RO processing. The study also showed that the presence of significant quantities of suspended materials or iron cause operational problems which limit the success of RO processing under these conditions. When these conditions exist at a spill site, more extensive pretreatment than simple prefiltration would be required.

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UNIQUE HAZARDOUS MATERIAL SPILL CONTROL AGENTS AND METHODS OF APPLICATION

JOHN F. RILEY, Ph.D.
ANSUL FIRE PROTECTION
WORMALD U.S., INC.

The purpose of this paper is to describe a technology for treating spills of hazardous materials. This technology is based upon three new solid formulations for treating spills of hazardous acids, caustics or organic liquids. The materials are applied using a mechanical applicator that is similar to a cartridge type fire extinguisher.

The market for hazardous waste material is estimated to 280 million metric tons/year in the United States.[1] Of this only 5% is treated off site at non-generator licensed treatment, storage, disposal facilities (TSDF's). In a private market survey conducted by the Ansul Company some interesting conclusions were obtained. This survey was sent to 5000 persons with designated responsibilities in environmental quality, environmental engineering or environmental management, industrial hygiene or safety. Responses were obtained from 1800 for a 36% response. The 5000 person sample covered several different industries ranging from food and beverage processing through petroleum and petrochemical. The average spill size as a result of this survey was determined to be 11.0 gallons and the frequency of spills was determined to be 8 spills per year per plant. The locations within the plant when spills occur is given in Table 1.

TABLE 1 DISTRIBUTION OF SPILLS IN THE PLANT

Shipping	9%
Recovery	8%
Warehouse	11%
Manufacturing	30%
Process Piping	14%
Tank Storage	17%
Labs	10%
Off site transport	4%

The data clearly indicates that the majority of spills occurs in the manufacturing process area. Based on the information developed through analysis of this information, spills of hazardous materials of up to a few hundred gallons were targeted as occurring most frequently and causing significant business interruption.

Hazardous materials and wastes are regulated by the U.S. Environmental Protection Agency (EPA) under the Resource Conservation Recovery Act (RCRA) as amended November 1985. Hazardous materials and wastes are those that exhibit one or more of the following properties.[2]

Corrosive	pH less than 2.0 or greater than 12.5

Ignitable	Peusky-Martens Closed Cup Flash Point of less than 140°F (60°C)
Reactive	Thermal or mechanical or chemical reactivity
Toxicity	Poisons, Carcinogens, Teratogens and Mutagens

Materials exhibiting one or more of these properties are considered hazardous and their treatment, storage and disposal are regulated by the EPA. Because of the above definitions hazardous materials can be broken down into these broad classes.

- Mineral and Organic Acids
- Caustics and Organic Bases
- Organic Solvents and Fuels

Using these broad classes, solid formulations were developed to affect both neutralization and solidification[3] of acid or caustic hazardous materials or wastes and the solidification of organic solvents and fuels as well as elevation of the flash point above 60°C (140°F). While the chemistry to achieve these goals is relatively simple, the reduction to practice is complex.

Neutralization and solidification of acids and bases includes a simple acid-base reaction:

$$\text{Acid and Base} \longrightarrow \text{Salt} + H_2O + \Delta H$$

where ΔH represents the heat of neutralization. However this can be a violent reaction with spattering, off gasing (fuming) and uneven heat generation. To avoid this formulations were developed to eliminate spattering and off gasing and minimize the uneven heat generation. For the acid formulation, a combination of Group I carbonates and Group II oxides was found to give the most effective and most rapid neutalization and solidification. The formulation also contained clays for moisture absorption and a surface treatment to render the mixture hydrophobic and also improve its flow characteristics.

The casutic or base formulation consists of a mixture of tricarboxylic and di-carboxylic acids with clay and a surface treatment. In the case of the acid and caustic formulations the neutralization and solidification process takes about 15 minutes after which the pH is determined prior to barreling and disposal. The disposal is then done in accordance with federal, state, provincial or local regulations.

Sulfuric acid (95%) was used as the bench mark for the acid formulation. The objective for effectiveness was 1 lb. of agent per pound of spilled material. Table 2 lists all of the acids that were tested with the acid formulation and at what concentration as well as how much agent was required per gallon of spilled acid. Table 3 is a summary of the results obtained for caustics when they were tested with the base formulation. As the data indicates, the target rate of 1:1 was met except where there was not chemical equivalence. The monoprotic acids resulted in a ratio of about .80, whereas the triprotic acid H_3PO_4 required a ratio of 1.20. Table 4 shows the difference in volume of acid either just neutralized or un-neutralized and solidified using a Model SC-30A applicator. The applicator contains 30 lbs. of the acid formulation. Returning to Tables 2 & 3, it can be seen that the 30 lb. applicator will neutralize and solidify about 2.5 gallons of acid whereas the 150 lb. applicator will do the same for about 12.5 gallons. The 350 lb. applicator will handle about 30 gallons of spilled acid. In examining the data on caustics, it would appear that two groupings are present. One group is the organic bases where the volumes treated are 1 gallon, about 4 gallons and about 10 gallons. The inorganic bases or caustics show much more depending on concentration than did the inorganic acids in Table 4.

The third formulation developed was for organic fuels and solvents. The approach taken here was to screen a number of activated carbons and select the best one in terms of adsorptive capacity, ability to reduce evaporation rates and ability to elevate the flash point above 140°F (60°C). A special activated carbon was selected which was derived from a metallurgical grade of coal having a surface area of between 1300 and 1500 m^2/gm (about .25 sq. miles/lb.). Table 5 is the data collected on over 50 organic fuels and solvents. Thus if 2.2 gallons of acetone were spilled it would required 11 lbs. of agent to adsorb it, 21 lbs. to reduce the evaporation rate and an additional 23.75 lbs. to elevate the flash point above 104°F (60°C) or a total of 44.75 lbs. The effectiveness objective was 1 lb. of agent per lb. of spilled liquid and this objective was by and large met.

The above formulations also had to be prepared having certain physical properties since they were to be delivered to the spill by a pressurized container similar to a dry chemical fire extinguisher. The two key properties here are bulk density and particle size distribution. Bulk density is a measure of the volume occupied by a given weight of a material. Particle size distribution is a measure of how particles of different size are distributed in a representative sample. The acid formulation has a bulk density of 95 cm^3/100 gms or .98, the caustic formulation has a bulk density of 115cm^3/100 gms or 1.15 and the organic formulation has a bulk density of 225 cm^3/100 gn ir 2,25. In a practical sense this means that in a 30 lb. hand portable applicator, 30 lbs. of the acid formulation, 25 lbs. of the caustic formulation and 11 lbs. of the organic formulation could be charged into the applicator.

The method of application that works the best is to approach the spill from the up wind side if possible, wearing the appropriate protective equipment and start applying the agent at a distance of 6-8 ft. at the perimeter. This will begin to establish control of the back lag forming a dike. This procedure should be followed around the perimeter until the spill has been completely diked. Then agent should be applied inward until all of the liquid has been covered.

TABLE 2

SPILL-X-A AGENT APPLICATION QUANTITY

TYPE OF ACID AND % CONCENTRATION			NEUTRALIZATION AND SOLIDIFICATION SC-30-A APPLICATOR* gal.	(L)	SC-W-150-A APPLICATOR* gal.	(L)	SC-W-350-A APPLICATOR* gal.	(L)	TREATED MATERIAL FORM AFTER 15 TO 30 MINUTES OF COOLING
ACETIC	99%	(17.4 Molarity)	2.50	(9.5)	12.50	(47.3)	29.17	(110.4)	Solid
FORMIC	90%	(23.3 Molarity)	2.50	(9.5)	12.50	(47.3)	29.17	(110.4)	Solid
HYDROCHLORIC	36%	(12.0 Molarity)	2.50	(9.5)	12.50	(47.3)	29.17	(110.4)	Solid
HYDROFLOURIC	49%	(28.4 Molarity)	2.50	(9.5)	12.50	(47.3)	29.17	(110.4)	Paste
NITRIC	70%	(15.9 Molarity)	2.50	(9.5)	12.50	(47.3)	29.17	(110.4)	Solid
PERCHLORIC	70%	(11.7 Molarity)	2.50	(9.5)	12.50	(47.3)	29.17	(110.4)	Solid
PHOSPHORIC	75%	(12.0 Molarity)	2.50	(9.5)	12.50	(47.3)	29.17	(110.4)	Solid
SULFURIC	93%	(17.4 Molarity)	2.25	(8.5)	11.25	(42.6)	26.25	(99.4)	Solid

* The SC-30-A hand portable applicator contains 30 lb. (13.6 kg) of SPILL-X-A agent.
The SC-W-150-A wheeled applicator contains 150 lb (68 kg) of SPILL-X-A agent.
The SC-W-350-A wheeled applicator contains 350 lb. (158.8 kg) of SPILL-X-A agent.
The 5 gal. pail holds 50 lb. (22.7 kg) of SPILL-X-A agent.
The fibredrum holds 200 lb. (90.7 kg) of SPILL-X-A agent.

TABLE 3
SPILL-X-C AGENT APPLICATION QUANTITY

TYPE OF CAUSTIC	NEUTRALIZATION/SOLIDIFICATION SC-30-C APPLICATOR* gal.	(L)	SC-W-150-C APPLICATOR* gal.	(L)	SC-W-350-C APPLICATOR* gal.	(L)	TREATED MATERIAL FORM AFTER 15 TO 30 MINUTES OF COOLING
AMMONIUM HYDROXIDE (29%)	4.33	(16.4)	20.09	(76.0)	49.36	(186.8)	Liquid Slurry
DIMETHYL FORMAMIDE	.70	(2.6)	3.25	(12.3)	7.98	(30.2)	Solid
POTASSIUM HYDROXIDE (45%)	2.87	(10.9)	13.30	(50.3)	32.72	(123.9)	Liquid Slurry
PYRIDINE	.95	(3.6)	4.41	(16.7)	10.83	(41.0)	Solid
SODIUM HYDROXIDE (50%)	1.80	(6.8)	8.34	(31.6)	20.52	(77.7)	Paste

* The SC-30-C hand portable applicator contains 25 lb. (11.3 kg) of SPILL-X-C agent.
The SC-W-150-C wheeled applicator contains 116 lb. (52.6 kg) of SPILL-X-C agent.
The SC-W-350-C wheeled applicator contains 285 lb. (129.2 kg) of SPILL-X-C agent.
The 5 gal. pail holds 42 lb. (19.1 kg) of SPILL-X-C agent.
The fibredrum holds 168 lb. (76.2 kg) of SPILL-X-C agent.

TABLE 4
ACID CONCENTRATION TREATMENT TABLE

TYPE OF ACID AND % CONCENTRATION		NEUTRALIZATION ONLY SC-30-A APPICATOR* (pH 5 - 9) gal.	(L)	NEUTRALIZATION AND SOLIDIFICATION SC-30-A APPLICATOR* gal.	(L)
SULFURIC	95%	3.20	(12.1)	2.25	(8.5)
	70%	5.90	(22.3)	2.20	(8.3)
	50%	5.90	(22.3)	3.10	(11.7)
	30%	10.20	(38.6)	4.70	(17.8)
	10%	13.00	(49.2)	3.20	(12.1)
HYDROCHLORIC	37%	10.80	(40.9)	2.60	(9.8)
	30%	10.80	(40.9)	2.20	(8.3)
	25%	14.70	(55.6)	2.30	(8.7)
	20%	16.20	(61.3)	2.20	(8.3)
	15%	18.00	(68.1)	2.30	(8.7)
	10%	21.50	(81.4)	2.90	(11.0)
ACETIC	99.7%	8.90	(33.7)	2.50	(9.5)
	70%	10.50	(39.7)	3.70	(14.0)
	50%	15.50	(58.7)	3.00	(11.4)
	30%	16.20	(61.3)	2.30	(8.7)
	10%	32.40	(112.6)	2.70	(10.2)

TABLE 5

TYPE OF SOLVENT OR FUEL	FLASH POINT °F	(°C)	ADSORPTION PER SC-30-S APPLICATOR gal.	(L)	ADDITIONAL SPILL-X- AGENT TO REDUCE EVAPORATION lb.	(kg)	in.	(cm)
ACETONE	0.0	(-17.7)	2.20	(8.3)	21.00	(9.5)	4.00	(10.2)
AVGAS 100	-46.0	(-43.3)	1.65	(6.2)	12.00	(5.4)	2.25	(5.7)
GASOLINE, UNLEADED	-40.0	(-40.0)	1.75	(6.6)	12.00	(5.4)	2.25	(5.7)
HEPTANE	25.0	(-3.9)	1.12	(4.2)	15.00	(6.8)	2.75	(7.0)
HEXANE	-7.0	(-21.7)	1.65	(6.2)	22.00	(10.0)	4.25	(10.8)
ISOPROPYLALCOHOL	53.0	(11.7)	1.65	(6.2)	6.00	(2.7)	1.25	(3.2)
METHANOL	52.0	(11.1)	1.65	(6.2)	12.00	(5.4)	2.25	(5.7)
TOLUENE	40.0	(4.4)	1.32	(5.0)	12.00	(5.4)	2.25	(5.7)
1,1,1-TRICHLOROETHANE	N/A	N/A	2.20	(8.3)	13.50	(6.1)	2.50	(6.4)
1,1,2-TRICHLOROETHANE	N/A	N/A	1.40	(5.3)	33.00	(15.0)	6.25	(15.9)

TYPE OF SOLVENT OR FUEL	ADDITIONAL SPILL-X-S AGENT TO ELEVATE FLASH POINT ABOVE 140°F (60°C) lb.	(kg)	in.	(cm)	ADDITIONAL SPILL-X-S AGENT TO REDUCE EVAPORATION AND ELEVATE FLASH POINT ABOVE 140°F (60°C) lb.	(kg)	in.	(cm)
ACETONE	23.75	(10.8)	4.50	(11.4)	44.75	(20.3)	8.25	(21.0)
AVGAS 100	6.00	(2.7)	1.25	(3.2)	18.00	(8.2)	3.50	(8.9)
GASOLINE, UNLEADED	2.00	(0.9)	.50	(1.3)	14.00	(6.4)	2.75	(7.0)
HEPTANE	10.00	(4.5)	2.00	(5.1)	25.00	(11.3)	4.75	(12.2)
HEXANE	12.00	(5.4)	2.25	(5.7)	34.00	(15.4)	6.25	(15.9)
ISOPROPYLALCOHOL	23.00	(10.4)	4.25	(10.8)	29.00	(13.2)	5.25	(13.3)
METHANOL	68.00	(30.8)	12.50	(31.8)	80.00	(36.3)	14.50	(36.9)
TOLUENE	5.00	(2.3)	1.00	(2.6)	17.00	(7.7)	3.25	(8.3)
1,1,1-TRICHLOROETHANE	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1,1,2-TRICHLOROETHANE	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

In the case of acids and caustics it is necessary to stir up the solidified material to ensure that the material is completely neutralized. The pH of a representative sample must be determined before any attempt is made to dispose of the material. In most cases involving acids or caustics, the resulting salt will have a pH greater than 2.0 or less than 12.5 and can be disposed of in accordance with local, state, provincial or federal regulations.

The applicators were modified external expellent gas cartridge fire extinguishers. The major modifications were in the ratio of gas to solids, the nozzle, operating instructions and color coding. The applicators ranged in size from 30 lbs. to 5000 lbs. in hand portable, wheeled and stationary configurations. The latter are available in both hand hose line and fixed pipe configuration.

In summary a novel approach to treating spills of hazardous materials has been developed. These different formulations have been developed for treating acids, caustics and organic solvents and fuels. In most cases these materials react to render a hazardous material into a non-hazardous material. These formulations are mated with external expellent gas cartridge applicators ranging in size from 30 lbs. to 5000 lbs. This results in a safe, fast way of reacting to and treating spills of hazardous materials.

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COUNTERMEASURES FOR CHEMICAL SPILLS IN THE NORTH THOMPSON RIVER

L.B.Solsberg

Counterspil Research Inc.
West Vancouver, British Columbia

INTRODUCTION

Countermeasures were investigated for controlling accidental releases from railroad cars of ammonia, ethylene dichloride, sodium hydroxide and styrene into the North Thompson River, British Columbia. The study was part of a project undertaken to develop a computerized hydraulic model for the river and, by analyzing chemical spill scenarios, to identify their possible environmental impacts. Planning the means to minimize these effects was the purpose of this study.

The four substances of concern were selected for examination because they are transported on a regular basis by rail to the Vancouver area. Moreover, they encompass a wide range of physical and chemical properties having varied implications on the fate, effects and cleanup of the hypothesized discharges. The group is comprised of a floater, a sinker and two mixers; two are flammable; usual shipping states include a liquefied gas and liquids; and factors such as pH, reactivity with water, temperature and toxicity figure differently for each chemical. Such behavioural data should allow application of the model and projected countermeasures to other substances.

The approach taken was to first review the properties of the four chemicals of most relevance to spill response and then to identify and assess promising cleanup techniques according to a synthesis of the current literature. Materials compatibility information, spill manuals and technical papers were consulted during the course of this work. What has resulted is an analysis of spill control hardware and materials to deal with ammonia, ethylene dichloride, sodium hydroxide and styrene organized according to the following subject areas:

- CONTAINMENT
  - Leak Mitigation and Vapour Control
  - Containment on Land
  - Containment in Water
- REMOVAL
  - Removal from Land
  - Removal from Water
- TEMPORARY STORAGE
- TRANSFER
- ULTIMATE DISPOSAL
- WINTER OPERATIONS

The response operations studied are indicative of an ordered series of cleanup phases that would have to be considered to deal with a spill. Strategies are based on predictions of what might occur and, therefore, might not always apply to any given event. Each situation would have to be carefully assessed according, but not limited, to the nature and volume of the release, its location, seasonal concerns and available countermeasures.

In the latter regard, many treatment methods and systems are noted in the literature that are at the conceptual, laboratory-scale or prototype stage only or that have undergone limited evaluation. While this paper summarizes the groundwork for selecting cleanup gear, undoubtedly, engineering design will have to be conducted prior to using the technologies discussed.

Materials compatibility specifically requires close scrutiny. Pertinent data can be derived from selection charts for protective clothing, laboratory ware, pumps, hoses, membranes, etc. As this implies, each item contacting a chemical must be chosen based on its individual application. It cannot be assumed, for example, that a polymeric recommended as a liner will provide satisfactory service as a pump seal for the same substance. Different solution strengths must also be considered.

Finally, it should be emphasized that while preplanning chemical spill countermeasures can significantly facilitate cleanup, advice at the accident scene from the chemical manufacturer and other experts can eliminate many of the unknowns--and dangers.

AMMONIA

Behaviour

Anhydrous ammonia is usually shipped under pressure as a liquid. If spilled, vaporization occurs and aerosols form so that the vapour cloud travels close to the ground. Ammonia will float, boil and dissolve to a significant extent when released into water. Explosive mixtures can develop when the gas is partially enclosed. Aluminum, brass, copper and galvanized steel are corroded by the gas while some plastics and rubber as well as many other chemical commodities react with it. It is toxic by inhalation and ingestion and corrosive to body tissues.

Personal protection, fire and vapour control are likely to be first priorities for accidents involving discharges of ammonia. Emergency guides should be consulted for pertinent directives.

Containment

Where feasible to consider, medium-to-high expansion surfactant-base foams that are alkaline resistant might be used to reduce fire hazards immediate to the accident site as well as downwind concentrations. This approach, however, is less likely in remote regions along the Thompson River. Firefighting equipment would have to be quickly obtained and might not be readied in time to control the high rate of vaporization that is likely to be encountered. Water spray could also provide effective vapour control, if containment of contaminated runoff were possible, and it is the method of choice for the rural area of concern.

Lower volume leakages from small openings might be halted by plugging systems manufactured by Edwards and Cromwell, Plug N'Dike, and Rockwell or by innovating equivalent devices in the field using polyester or chloroprene rubber (Neoprene) materials. The Tantalum Patch Kit incorporates inappropriate substances and typifies the care that should go into selecting plugs.

Containing ammonia solutions on land should be readily accomplished. Compacted earthen dykes, formed (ideally) from a high clay content soil, would serve as effective barriers. Most types of synthetic membranes, with the exception of butyl rubber, could be considered as a liner to further reduce the liklihood of contaminated water reaching the Thompson River.

Synthetic foam systems are sold by various manufacturers such as MSA and Lusta-Foam which can be utilized to instantaneously fabricate barriers on land. Such lightweight impervious structures seem to be of less practical value than the construction of earthen dykes using heavy, earth-moving equipment although more limited containment, storage or other cleanup work might benefit from their very mobile, fast format. One cautionary note is that labware catalogues list polystyrene and polyurethane foams as being less resistant to solutions of ammonium hydroxide.

Containment of ammonia spills in the Thompson River and tributary streams will not usually be feasible because of ammonia's high water solubility. For small creeks, when circumstances permit, it might be possible to devise semi-permable barriers from chicken wire, posts, straw bales and sorbents to retain some contaminant.

Removal

Aqueous solutions of ammonia contained on land could be removed by direct pumping. Transfer systems should be utilized that do not incorporate bronze, zinc alloy (galvanized), aluminum or PVC shafts or casings. Viton seals are to be avoided. Centrifugal pumps made by various manufacturers are applicable including cast, stainless, phenolic and epoxy models featuring Neoprene seals and impellers. Suitable transfer hoses and fittings can be obtained fabricated from a variety of synthetic materials.

Sorbents can be used effectively to deal with minor amounts of ammonia solution lying on the ground. Conwed, Absol, Hazorb and Cellosize are several of the commercial products that can be purchased to remove small volumes.

Gelling agents are also sold which, theoretically, can immobilize ammonia solutions. The approach is not seen to be a practical alternative. Gelling is relatively expensive, it requires a secondary cleanup phase and, as such, it is not nearly as direct a method as pumping, paricularly for the Thompson River corridor.

Once ammonia has entered the groundwater, interceptor wells or trenches might have to be constructed to remove contaminant. Difficulties are likely to be encountered since ammonia will assume the direction of flow of the water and could ultimately find its way into the Thompson River regardless of such attempts.

Where penetration into the ground has occurred yet the spill is more localized, excavation of materials might be necessary. Treatment might also be possible. Dilution-neutralization-filtration using water, hydrochloric and sulfuric acids can be set up at the spill site if a longer-term cleanup is warranted. Potassium chloride solution could also be injected to free chemically-bound ammonia which would then require removal by aeration. Air and steam stripping hold some promise to deal with ammonia spills onto land. Air emission regulations must then be complied with, a factor that has hampered past cleanup attempts.

Environment Canada's reverse osmosis unit also could be used to concentrate aqueous solutions of ammonia resulting from either the knockdown of vapours by water spray or from dilution by groundwater. The portable RO unit facilitates cleanup by reducing the volume of waste that must be subsequently transferred.

In the case of ammonia discharges into smaller streams, time will not generally allow effective implementation of treatment. Neutralization might be attempted using hydrochloric acid or sodium dihydrogen phosphate. Problems with this approach along the Thompson River and its tributaires include the difficulty in determining appropriate interception points as well as in calculating precise volumes of treating agent to apply.

Temporary Storage

Storage of collected ammonia solutions should not pose a problem. With the exception of the metals already indicated, including aluminum and galvanized steel, and synthetics such as butyl rubber, many storage systems fabricated in standard materials could be employed. Tank trucks and cars, flexible and rigid tanks, and lined pits or trenches could all be used as needed.

Transfer

A primary method for recovering spilled ammonia will be the pumping of aqueous solutions using transfer hardware. All associated components and fittings should be selected with care including the pump casings, shafts, seals, connectors and hoses. Consultation with experts is recommended, particularly in overseeing the transfer of anhydrous ammonia from damaged railcars. Generally, bronze, aluminum, PVC, nitriles and Viton are to be avoided for some operations, depending upon the pumping component, temperature, and the concentration of the solution.

Ultimate Disposal

Ideally, all ammonia-contaminated water should be forwarded to a waste management faciltiy for processing. On-site treatment using the RO unit, air stripping and steam extraction to recover and concentrate solutions should simplify transfer logistics.

A landfarming operation could be implemented in the Thompson River area to dispose of solid and/or liquid wastes. Nitrifcation and plant uptake can proceed once mixing with soil has taken place along with the proper management of pH and water content.

Winter Operations

Where entry of ammonia into groundwater and the Thompson River is prevented by ice cover, an obvious advantage would be gained. During winter, spill control through vapour suppression might be possible using a snow blower. Snow might also be used as a sorbent with front-end loaders and dump trucks brought in to both contain and remove spilled material. It is unrealistic not to expect a range of difficulties imposed by cold weather including engine start-up problems, freezing of pumps, restricted access to the accident scene and the discomfort of personnel.

ETHYLENE DICHLORIDE

Behaviour

Ethylene dichloride is a flammable liquid that can form explosive mixtures in air and flash back along vapour trails. Toxins are often produced as the result of fires. Evaporation occurs at slow rates. It reacts violently with ammonia and aluminum as well as many oxidizers. In water, ethylene dichloride dissolves slowly and sinks while not hydrolyzing or otherwise reacting. Lethal concentrations might be present in the Thompson River many kilometres downstream from the original point of discharge.

Fire prevention and control as well as personal protection are accident response priorities. Consult emergency guides for requirements on self-contained breathing apparatus and clothing.

Containment

Smaller fires can be controlled with AFFF/alcohol foams, dry chemical, CO_2 or water spray. Vapour control can be achieved simultaneously. Foams and water spray will also extinguish larger fires, with water serving to cool containers and reduce hazards.

Smaller punctures can be plugged when this is safe to do so using devices from Edwards and Cromwell, Vetter (sealing bag), Rockwell (leak plugger with appropriate applicator tip), NRC (Tantalum patch kit) and Plug N'Dike.

Containment of spills on land that borders the Thompson River should be possible through the construction of earthen barriers. Compacted soils high in clay content and liners will render dyking impervious to leakages. A number of materials should be avoided if these are in contact with ethylene dichloride: natural rubbers, Neoprene, nitrile/butyl rubbers, Hypalon, chlorinated polyethylene (CPE), ethylene propylenediene monomer (EDPM) and PVC. These should also not be used in the storage of materials.

There are problems inherent in trying to contain ethylene dichloride released in the Thompson River and its tributaries. The chemical sinks and dissipates according to local hydraulic forces. Halting migrations toward or at the bottom of water courses and removing contaminated sediments are concerns.

Mechanical containment might be possible in smaller side streams where a weir and overflow device can be devised to trap materials flowing at or toward the stream bed. Accumulations might result where pooling occurs naturally or by the use of sand bags or other means. The type of semi-permeable barrier noted to control ammonia spills might also be tried for ethylene dichloride, i.e. a flow-through device made from chicken wire/posts/straw bales/sorbent. Activated carbon contained in mesh bags and sorbents that have been weighted might achieve the same results.

In the Thompson River, containment is likely to be less feasible. Still, it might be possible to select wider, shallow, more slowly flowing river reaches where spilled material hugging the bottom would tend to deposit. Positioning sandbags at the river bottom could then be tried either perpendicular to the flow or angled toward an embayment (as one would place a deflection barrier on the water's surface to reduce the relative current velocity) to divert contaminant for subsequent mechanical recovery.

Removal

Pumping spilled product that has pooled on land should be a relatively uncomplicated procedure employing standard transfer systems and vacuum units (see also Transfer). To remove minor accumulations, sorbents could be used including sand, Absol, Safestep, Imbiber beads, Hazorb and activated carbon materials. Sorbents should immobilize the contaminant to facilitate its mechanical removal. Gelling agents would likely achieve the same effect with ethylene dichloride--more so than with ammonia--but their cost, efficiency of application and secondary cleanup requirements still leave their use questionable.

When penetration into the ground has occurred, removal of ethylene dichloride becomes a more involved task. Excavation of materials would proceed where the spill was localized in a small area. A primary problem, however, relates to the chemical's tendency to move downward through sandy and coarse grain soils. It would not float on the water table as a hydrocarbon fuel would. Any prescribed physical/chemical treatment might therefore be difficult to implement with high recovery efficiencies.

Air stripping, which was tried at a recent spill of ethylene dichloride in British Columbia, in-situ oxidation using ozone or air sparging, surfactant injection, and solvent extraction have been determined to be either relatively ineffective (in the case of the air/ozone oxidation/stripping methods) or to be procedures requiring complex processing equipment (such as the EPA trailer).

Since steam stripping holds some promise, Environment Canada is planning to investigate it further. Wet air oxidation also has good potential to treat such wastes and it has been developed thus far as a fixed facility installation and as a prototype mobile processor. UV-oxidizing units appear to be less effective. Carbon adsorption systems, such as Calgon's mobile water treatment unit, are commercially available and could be transported to accident sites adjacent to the Thompson River. Both single-stage powdered carbon contactors and granular carbon columns should be capable of removing ethylene dichloride from groundwater. Concentrations of 0.1 to 10 ppm should be amenable to treatment at removal efficiencies exceeding 80%.

Higher concentrations of 100 to 1000 ppm might eventually be recovered using the Environment Canada RO unit; however, further research is required to develop a compatible membrane and incorporate appropriate hardware such as Viton seals and stainless steel fittings. It is also possible that groundwater treatment of ethylene dichloride might entail the utilization of multi-step processing inclusive of RO, steam stripping, carbon adsorption, alcohol extraction and/or recycling. Environment Canada has also indicated pending studies of molecular sieves.

In the smaller tributary streams along the Thompson River, sorbents might be used to pick up minor amounts of released material. Dredging, pumping and suction techniques could also be used, where appropriate, to remove contaminated sediments and bottom accumulations. The treatment systems with more promise, as discussed above, might also be of use in smaller water courses.

In the Thompson River, a smaller volume discharge would probably dissipate to the point where physical/chemical treatment was not practical. Larger spills resulting in localized contamination might allow the effective use of mechanical means such as sludge handling and dredging systems. The entrapment of bottom materials through the use of angled barriers might enhance such cleanup. Treatment of contaminated Thompson River water is seen to be less useful. Weighted sorptive barriers are similarly viewed with less favour, mainly due to fouling and hydraulic problems.

Temporary Storage

Tank trucks and cars, trenches, flexible containers and rigid-wall units could all be applied to temporarily hold collected ethylene dichloride. Closed containers should be considered if vaporization is to be prevented. As pointed out, natural, butyl and nitrile rubbers should be avoided as well as synthetics such as Hypalon, CPE, EDPM and PVC. Aluminum containers are also not recommended versus steel and polypropylene materials.

Transfer

Pumps have to be carefully selected for transferring ethylene dichloride, a flammable liquid that could also, after being spilled, contain suspended solids. Environment Canada recommends single-suction, magnetic drive units with centrifugal impellers and wet-end construction in steel or stainless. A large number of pumps are commercially available that are sold for use with ethylene dichloride including teflon and polypropylene units.

Pumps should be used without synthetic rubber components nor aluminum, phenolic and PVC bodies and shafts. Screw connections should be avoided. Flanges at suction and discharge ends, and drain plug and self-priming should be features.

Hose types involve a similar selection process that takes into account the solvent action of ethylene dichloride.

Ultimate Disposal

Ethylene dichloride should be disposed of in an approved type of combustion chamber equipped with vent control. Treatment systems are not generally available in the Lower Mainland area that could be used to process the waste materials in question. Placement in a sanitary landfill site is an option, particularly if the waste has been stabilized through fixation techniques.

Winter Operations

Colder temperatures would reduce the rate of vaporization of ethylene dichloride along with fire hazards. Snow could be blown to knock down any vapours but would not act as a sorbent due to the chemical's low water solubility. Snow and ice barriers could halt the flow of contaminant where this is feasible to undertake. The freezing point of ethylene dichloride at -36°C might be reached, necessitating the application of solids handling equipment but otherwise reducing the overall hazard.

SODIUM HYDROXIDE

Behaviour

Sodium hydroxide is usually shipped in tank cars as 50% and 73% solutions which are both highly corrosive, toxic by ingestion, and reactive with many other substances. The 50% format is a liquid at ambient temperature while the 73% concentrate is gelatinous. Dissolution in water will generally occur rapidly with the evolution of heat. Some material might remain afloat before finally mixing until it is diluted. Sodium hydroxide neither burns nor supports combustion. Once it has entered the Thompson River, dilution will occur to sub-toxic levels as it is transported downstream and disperses. Toxic effects on aquatic organisms can be expected in the vicinity of the release point.

Consult emergency guides for information on protective clothing.

Containment

Vapour control should not be a concern although inhalation of particulates is to be avoided. Caustic should be prevented from contacting some metals including bronze, brass, tin and aluminum because hydrogen might be generated creating an explosion hazard.

For smaller punctures of tank cars, temporary repair could be effected using various available materials (see also Storage) and the plugging devices noted for ammonia and ethylene dichloride, with the exception of the NRC Tantalum Patch.

Earthen barriers formed from compacted, high clay content soils could be constructed to intercept spillages on land, if response time permits this approach. Most synthetic membranes could be used as liners although PVC is likely to deteriorate upon prolonged exposure. Water saturation of the ground, and the penetration of caustic into it, should be avoided in the vicinity of the accident site. The 73% concentrate should not normally present containment problems on land due to its gelatinous form.

Once sodium hydroxide has entered the Thompson River or any of its tributary streams, containment will be unlikely due to its propensity to rapidly dissolve and mix. Damming, water diversion and semi-permeable barriers are seen to be of very limited use.

Removal

Solutions of sodium hydroxide contained on land should be pumped using equipment suitable for caustic service. This generally means to avoid the utilization of bronze, phenolic and PVC pump bodies as well as nitrile and Viton impellers and seals (see also Transfer). Front-end loaders, graders, scrapers and shovels could be used to recover the gelatinous form although some corrosion of steel will occur and should be expected or avoided as warranted.

Various sorptive materials will immobilize minor amounts of spilled caustic solution. Non-commercial sorbents include sand, clay, fly ash, vermiculite and cement powder. Commercial products that could be applied include Absol, Hazorb, Safestop, Spill Control Pillows and Spill Clean. The spent sorbent would then have to be retrieved using mechanical means as is noted above.

Chem-Gel or other gelling agents could also be used to agglomerate and control the spreading of sodium hydroxide but their utilization, as has been previously discussed, appears to be less practical than the application of pumps.

Once penetration into the ground has occurred, excavation and/or neutralization might be tried. The latter would include the addition of sodium dihydrogen phosphate, acetic acid or dilute hydrochloric acid. Interceptor trenches might also prove feasible to construct if contaminated groundwater can be made to flow into these. Generally, however, the solubility of sodium hydroxide will result in its bypassing trenches or any treatment methods if it contacts groundwater.

Removal of sodium hydroxide spilled into water is, at best, a difficult task. Retaining the contaminated water of smaller tributary streams might be possible using damming techniques but it is not an approach that would often provide satisfactory results. Pumping or the use of the RO unit might be considered for some situations. Using sorbents would be similarly limited.

Treatment would likely be considered to control spills. Sodium dihydrogen phosphate is the in-situ treating agent of choice for neutralizing releases of sodium hydroxide into waterways. It avoids the pH effects of overdosing with acetic and hydrochloric acids although the latter are often recommended in handbooks. J.T. Baker Chemical Company also produces a chemical agent that can be used to neutralize an alkali spill. It features a pH indicator which signals through colour change when the reaction has gone to completion. Interception points must still be planned to ensure intimate contact of the agent with the contaminant.

Other treatment approaches do not usually address the processing of bases, versus more toxic organics. This does not eliminate the possibility of devising treatment in the field including, for example, gravity separation/filtration of solids, neutralization, pH adjustment. Ion exchange is a less likely candidate because of its expense and more limited processing capacity.

Removal of spilled sodium hydroxide in the Thompson River will not be feasible because of rapid mixing and dilution.

Temporary Storage

Containers and associated hardware fabricated from a number of metals should be avoided for the storage of sodium hydroxide. These include aluminum, brass, bronze, copper, tin , cast iron and zinc. Synthetics not recommended include polycarbonate, fibre-glass reinforced epoxy and PVC. Mild steel containers, inclusive of tank trucks, can be employed in the cleanup of 50% concentrate but some metal consumption might result. Stainless 316 and Monel alloys would usually resist 73% concentrates at ambient temperatures as would nickel but not might be available.

Many synthetic materials should provide adequate service when used as portable flexible or rigid-wall tanks or as liners for pits and trenches constructed for interim storage purposes. It would be appropriate to use, for example, high and low density polyethylene, polypropylene, polyvinylidene fluoride, Teflon and polystyrene materials. Nitrile rubber, Neoprene and Viton would tend to deteriorate in some caustic solution strengths at various temperatures. Many commercial products are suitable for use.

Transfer

Pumps exclusively designed to move caustic include stainless and Alloy 20 gear units and, for certain situations, centrifugal models having an open impeller, Monel shaft and deep stuffing box. Connections for steam cleaning and drain plugs should be features. Gaskets should be fabricated from graphitized asbestos, Teflon and rubber. Bronze and PVC casings and nitrile, Viton and, at times, Neoprene impellers should be avoided. Various hoses suitable for transferring sodium hydroxide are available in materials that include natural rubber, Hypalon, polyethylene, polypropylene and flexible stainless steel.

Ultimate Disposal

Treatment of collected materials might be undertaken at the accident site or under the more controlled conditions of a waste management facility using acetic, dilute sulfuric or hydrochloric acid. Gravity separation of solids and filtration might be additional required steps. Sludge could be placed in a secure landfill site. Fixation using cement or lime-based techniques would reduce leaching induced by contact with acids.

Winter Operations

Heat evolution should be less violent than in water if released sodium hydroxide contacts snow. Local melting would occur but the spill should remain relatively confined, depending upon the terrain. A larger discharge might break through ice cover into the Thompson River and would be difficult to treat even using neutralization techniques. Siginificant solidification of the discharged material is likely to occur, however, requiring use of scrapers and front-end loaders to effect the necessary cleanup.

STYRENE

Behaviour

Styrene monomer is a flammable liquid that can polymerize with significant heat release at elevated temperatures and in the presence of acid and base catalysts including some soils. It is only slightly soluble in water and floats but still might reach toxic levels in the water column following a spill. Vapours can travel considerable distances to flash back or ignite. Container rupture can occur due to heat or reaction with other chemicals.

Personnel protection, and fire and vapour control are response priorities. Consult emergency guides for specific directives.

Containment

For smaller fires, dry chemical, CO_2, water fog and protein-based foams could be used as the extinguishing agent. Vapour control is possible using high expansion surfactant-based foams in low wind conditions. Water spray or foams will combat larger fires with water useful, in particular, to cool containers and disperse vapours and not so much to directly control flames.

Plugging small punctures should only be undertaken by trained crews wearing suitable protective equipment. Repair kits should not be utilized that rely upon a Neoprene or other synthetic rubber material e.g. the Vetter Sealing Bag or Edwards & Cromwell emergency package. The NRC Tantalum Patch Kit includes a Teflon gasket suitable for use as is the Rockwell External Leak Plugging system with its optional fluoroelastomer applicator tip. Polyvinyl alcohol materials are also resistant to styrene.

For spills on land that do not penetrate soil, earthen dykes constructed fron compacted soil or sand should provide effective containment when this is feasible to undertake. Many liners will not afford any improvement to such dyking, especially over the longer term. Trenching could be similarly tried.

Because styrene is slightly soluble and floats, efforts could be made to contain it on the Thompson River or its tributaries.

In smaller water courses, retention might be possible through the use of fencing backed by sorbent materials including peat, straw and polyurethane foam. A dam and sub-surface culvert could also be devised to retain the floating material as would various sorbent booms, e.g. SPC, 3M, Conwed and Drizit.

For larger volume releases into the Thompson River, commercial booms could be used if these incorporate materials not subject to the solvent action of styrene. Many barriers, however, feature PVC, polyethylene, Neoprene and nylon as standard components of their fabric or in other construction details. Degradation over time is a possibility if styrene is concentrated against such materials. Polyurethane might prevent deterioration of the boom if used in its fabric makeup and is available from a number of manufacturers. Polyvinyl alcohols are also known to be highly resistant to styrene but do not exhibit good abrasion, cut and puncture characteristics. Once properly selected, boom should be optimally deployed at preselected sites.

Removal

Safety permitting, large volumes of styrene contained on land could be removed by pumping. Centrifugal and gear units could be utilized constructed of materials other than copper alloys and phenolics and without rubber seals--see also Transfer. Vacuum trucks and smaller portable pumps would also be suitable for use.

Sorbent materials could be effectively applied to remove minor amounts of spilled styrene. Non-commercial sorptive materials include soil, sand, clay, fly ash, cement powder, peat moss, saw dust and straw. Polymerics such as polypropylene and cellulosic fibres, e.g. Conwed, would also provide satisfactory results.

Gelling agents such as Chem-Gel, amine carbamate and the US EPA material are known to be capable of immobilizing styrene but, as previously stated, comprise a less practical approach as compared with other available cleanup approaches.

When penetration into the ground has occurred, excavation of contaminated materials would be required. To recover styrene from groundwater, devices could be used capable of removing floating substances when placed in a monitoring or collection well drilled down to the water table. The Douglas Engineering Sentry and Oil Recovery Systems Filter-Probe could be used if these were without synthetic rubber and other polymerics as well as copper alloys.

Insofar as treatment is concerned, many systems could be tried to recover styrene. Calgon's mobile carbon adsorption unit could be transported to smaller tributaries, or used to remove contaminant from groundwater, with a relatively high rate of efficiency. Air stripping, using a vertical packed column, is another possible approach, particularly for the removal of a volatile chemical having low water solubility. A combination of carbon adsorption and air stripping, as marketed by Oil Recovery Systems, Inc., provides the advantages of both types of processing capability. Solvent extraction techniques should also offer equivalent recovery efficiencies but might require a more complex design process before implementation. Some chemical engineering of any unit brought in would be necessary to deal with factors pertinent to the circumstances of the spill.

Direct pumping, sorbent booms, carbon adsorption and air stripping could all be considered for use in smaller feed streams along the Thompson River. In the main river itself, mechanical skimming or pumping is seen to offer the best potential to effect higher volume recovery rates, safety permitting. Skimmers are recommended that do not incorporate components vulnerable to damage. For this reason, sorbent surface devices (e.g. rope mops, discs, fabric drum and belt units) or skimmers with rubber or synthetic parts should not be used as compared with all metal skimmers such as the Pedco, SLURP, Skim-Pak (in stainless) and Megator. Prior containment and concentration with a boom would provide the means to optimize physical recovery operations.

Temporary Storage

Tank trucks and cars, drums and other rigid containers could be used to store collected materials. Because of styrene's solvent action, flexible or fabric containerization as well as liners will likely see more limited application. Polyvinyl alcohol and polyurethane offer higher resistance in this regard while Viton and polyethylene provide somewhat less breakthrough capability.

Rigid-wall storage units should not incorporate copper and its alloys and should be closed to minimize the risk of vapour transport, ignition and polymerization (the latter possibly being induced by heat and light). Isolating styrene from oxidizing gases, chlorine and acids is an important consideration. A flash point of 32°C requires that safeguards such as temperature alarm systems be used in interim storage facilities.

Transfer

Standard pumps can be used to transfer styrene such as double-seal and single-suction, seal-less magnetic centrifugal units. These should be explosion-proof, have stainless wet end components, drain plug, and flanges at both suction and discharge ends. Features to avoid include phenolics and copper and its alloys in pump bodies and shafts, screw connections (because of possible leaks), and synthetic or natural rubber O-rings and gaskets with the exception of Viton. Running the pump against a closed discharge line could lead to heat build-up and ultimately to polymerization and should be avoided.

Various hoses can also be obtained compatible with styrene. These should avoid some synthetics in both exterior covering and interior lining. Since many hose types are not impervious to styrene, advice from the styrene supplier is recommended.

Ultimate Disposal

Incineration in controlled facilities is the preferred method so that complete combustion is achieved of all waste materials and toxic gases are not released. Atomization or the use of a flammable solvent will promote the combustion process. Reprocessing of contaminated styrene is unlikely although the manufacturer should be consulted in this regard. Efficient, mobile incinerators are available in the US that are capable of treating off-gases. Their use is unlikely at spills near the Thompson River unless longer-term cleanup is needed.

Wet air oxidation and bromination or other more exotic disposal means seen to be less practical. They are generally applied to dispose of more complex substances such as pesticides.

Fixation of styrene would be possible using a pozzolan such as fly ash or cementitious material. This would result in an innocuous waste that would be isolated from the environment if deposited in a secure landfill site. Landfarming could also be tried in the Thompson River area so that biodegradation is enhanced through the proper management of controlling factors such as mixing with soil, pH, and water content. Although high removal efficiencies for styrene are reported for this latter method, disposal by incineration appears to be more appealing.

Winter Operations

Cold weather will result in lower evaporation rates and reduced potential of flashback and polymerization. Mechanically blown snow could be used to suppress vapours or be compacted to form snow or ice barriers to retain releases but could not be used a sorbent. The entry of styrene into the Thompson River would be prevented by ice cover. Since styrene freezes at about 31°C mechanical removal equipment might be required where access to the accident site allowed implementation of this approach.

REFERENCES & ACKNOWLEDGEMENTS

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Mr Fred Beech of the Environmental Protection Service in West Vancouver and Mr. Merv Fingas in Ottawa are acknowledged for their support of this component study.

"U.S. ENVIRONMENTAL PROTECTION AGENCY, ENVIRONMENTAL RESPONSE TEAM'S INTEGRATED OCCUPATIONAL HEALTH AND SAFETY PROGRAM", TURPIN, RODNEY D., U.S. ENVIRONMENTAL PROTECTION AGENCY, ENVIRONMENTAL RESPONSE TEAM, EDISON, NEW JERSEY, 08837, USA.

INTRODUCTION:

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to On-Scene Coordinators (OSC), Regional Response Teams (RRT), EPA Headquarters, and Regional Offices, as well as other United States and foreign governmental agencies in the area of emergency environmental issues such as chemical spills and uncontrolled hazardous waste sites.

The paper briefly describes the Occupational Health and Safety Program at the U.S. Environmental Protection Agency and the Environmental Response Team's integrated program. This paper includes a description of the following portions of the ERT Program:

1. Training Requirements
2. Medical Surveillance
3. Health Maintenance
4. Policy Requirements
5. Record Keeping

AGENCY OVERVIEW:

EPA ORDER 1440 (OCCUPATIONAL HEALTH AND SAFETY MANUAL): This order establishes the Agency's Occupational Health and Safety (OH&S) overall program and the following are some of the major points of this order:

1. Establishes the Agency's OH&S Policy, Responsibilities, and Procedures;
2. Appoints the Assistant Administrator for Administration and Resources Management the senior management official for OH&S; and
3. Appoints the Director of Occupational Health and Safety Staff, Manager of the Agency's OH&S Program.

In addition to the overall Agency Policy (EPA Order 1440), the Occupational Health and Safety staff has issued the following orders which address specific phases of the Agency's Policy:

1.) EPA Order 1440.2 - Health and Safety Requirements for Employees Engaged in Field Activities
2.) EPA Order 1440.3 - Respiratory Protection
3.) EPA Order 1440.4 - Health and Safety Training Requirements for Mine Safety
4.) EPA Order 1440.5 - Qualifications and Training Requirements for Occupational Health and Safety Program Personnel
5.) EPA Order 1440.6 - Motor Vehicle Occupant Restraining Systems

EPA ORDER 1440.2 - HEALTH AND SAFETY REQUIREMENTS FOR EMPLOYEES ENGAGED IN FIELD ACTIVITIES (EFFECTIVE: JULY 12, 1982): This order establishes training requirements which must be obtained prior to field activities, and maintained annually.

The order specifies three levels (Basic, Intermediate, Advance) of training certification based on employees' job functions and the type of exposure. The following summarizes the three training levels and lists the specific training requirements:

1. Basic Level: This level is for field activity personnel that are not required to work within a hazardous material or chemical release area. It requires twenty four (24) hours of classroom training followed by three (3) days of on-the-job-training (OJT) within three (3) months of completing classroom instruction. Employees are required to receive this training prior to any field activity and obtain eight hours of annual refresher training.

   a.) Twenty four (24) hours of classroom instruction must include:

      1.) Employee rights and responsibilities
      2.) Nature of anticipated hazards
      3.) Emergency help and self-rescue
      4.) Vehicles-mandatory rules and regulations
      5.) Safe use of field equipment
      6.) Use, handling, storage, and transportation of hazardous materials
      7.) Personal protective equipment and clothing, use and care
      8.) Safe sampling techniques

2. Intermediate Level: This level is for all inexperienced hazardous waste spill field personnel. It requires thirty two (32) hours of classroom training followed by three (3) days of OJT within three (3) months of completing the classroom instruction. Employees are required to receive this training prior to any field activities, and obtain eight (8) hours of annual refresher training.

   a.) Thirty two (32) hours of classroom instruction must include:

      1.) The basic level courses - (24 hours), plus
      2.) Site surveillance, observation, and safety plan development
      3.) Use and decontamination of totally enclosed protective clothing and equipment
      4.) Use of field test equipment for radioactivity, explosivity, and other measurements
      5.) Topics specific to other identified activities

3. Advanced Level: This level is for all experienced hazardous waste/spill field personnel. It requires (40) hours of classroom training followed by three (3) days of OJT within three (3) months of completing the classroom instruction. Employees are required to receive this training prior to any field activities.

a.) Forty (40) hours of classroom instruction must be given on:

1.) The basic and intermediate level courses - (32 hours), plus
2.) Management of restricted and safe zones
3.) Rules for handling the press and VIP's
4.) Safe use of specialized sampling equipment

ENVIRONMENTAL RESPONSE TEAM PROGRAM:

While ERT's integrated health and safety program meets both Occupational Safety and Health Administration's (OSHA) and the Agency's requirements, the team finds itself being a pace setter rather than a follower. Since the ERT is an international hazardous material response team, and is dedicated to providing the safest and healthiest workplace, we frequently find ourselves addressing situations that other individuals have no experience with, let alone published protocols/standards. Therefore, the Team's Integrated Health and Safety Program is based on various potential exposures and is all inclusive. The program consists of the following requirements: policy, record keeping, medical surveillance, health maintenance, and training requirements.

POLICY: After the initial staffing (three employees) in October 1978, the team leader decided in January 1979, with the addition of four more team members, that the team's field protocols and techniques needed to be formulized. This was done in order to effectively protect team members during response at field activities where state-of-the-art Occupational Health and Safety Protocols were not being utilized.

This effort is the grandfather of the U.S. EPA OERR, Standard Operating Safety Guides, November 1984 and is reflected in OSHA's 29 CFR 1910.120, Hazardous Waste Operations And Emergency Response (December 1986 Interim Final Rule). In addition, the written team's policy requires each team member to be totally responsible for his actions in the area of Occupational Health & Safety and to practice the ERT's Occupational Health and Safety procedures, protocols, and/or techniques. In the event more stringent protocols are being followed by on-site personnel, ERT members are required to follow them. In short, the policy calls for no employee exposure without personnel protective equipment no matter how low the concentrations are reported.

RECORD KEEPING: In addition to the Training Certification, Medical Monitoring, and Fitness for Duty Statement records required by the Agency, ERT requires cardiovascular-stress fitness and exposure recorders to be maintained. The exposure records are entitled "Incident Safety Check Off Sheets".

The employee is required to state what chemicals they may be potentially exposed to and what protective clothing is applicable for their activity prior to departing. Once the response activity is completed, the responder is required to complete the second half of the form and record the same type of pre-response information only this time it is based on the employees on-site observations.

MEDICAL SURVEILLANCE: Again, the ERT's policy is quite specific as to the overall philosophy of medical monitoring. While the Agency has only limited criteria for monitoring Agency personnel, ERT's program more specifically addresses the needs of the hazardous material responder. For example, ERT's program calls for exams twice per year, a Board Certified Occupational Health Physician to review all abnormal results, and a cardio-vascular fitness test of the employee.

HEALTH MAINTENANCE: The team's overall Occupational Health and Safety Program is not only concerned about direct and/or indirect chemical exposure, but it is concerned with the employee's general health ranging from eating habits to fitness. The ERT Health Monitoring program provides the employee with both the opportunity and the incentive to participate in a Cardio-Vascular Fitness Program as well as a Modified Health Awareness Program.

Training: In addition to the team members being required to receive and maintain EPA 1440.2 training, ERT presents the following courses throughout the United States and most of the team members are required to make specific presentations:

1.) Personnel Protection and Safety, 165.2 (5 days);
2.) Incident Mitigation and Treatment Methods, 165.3 (5 days);
3.) Sampling for Hazardous Materials, 165.9 (3 days);
4.) Hazardous Materials Incident Response Operations, 165.5 (5 days);
5.) Hazard Evaluation & Environmental Assessment, 165.8 (4 days);
6.) Response Safety Decision-Making Workshop, 165.8 (4 days);
7.) Air Surveillance for Hazardous Materials, 165.4 (5 days).

For additional course information, contact:

Thomas C. Sell, Training Coordinator
U.S. Environmental Protection Agency
Environmental Response Team
26 West St. Clair
Cincinnati, OH 45268, USA
513-569-7537

CONCLUSION:

Since both emergency actions and long term remedial activities are required to prevent and/or reduce the impact of an incident on the public health and environment, hazardous material response personnel find themselves involved in an Occupational Health and Safety environment not normally addressed by other industries. The author hopes that other response personnel find this overview of the ERT Integrated Occupational Health and Safety Program both informative and useful.

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PERFORMANCE STANDARDS FOR CHEMICAL PROTECTIVE CLOTHING IN EMERGENCY RESPONSE*

Lieutenant Jeffrey O. Stull
U. S. Coast Guard
Office of Research and Development
Washington, D. C.

INTRODUCTION

Federal, state, local, and commercial response organizations use a variety of protective clothing items to protect their personnel during chemical spill incidents. These clothing range from outfits of overalls, gloves, and boots to totally-encapsulating suits. Chemical protective suits offer the highest level of protection and are used when the greatest chemical toxicity hazards are encountered. Despite the widespread use of chemical protective suits, few standards have been developed which are directly related to chemical protective clothing. The American Society for Testing and Materials (ASTM) has introduced new test methods for protective clothing. For example, the ASTM F23 Committee on Protective Clothing has established a testing procedure for measuring the chemical permeation resistance of clothing materials. Nonetheless, there are no comprehensive standards which specify garment and material performance requirements.

The consequences for this lack of standards are multifold. Protective clothing users are faced with myriad of products in selecting the "right" garment. Many times, smaller organizations have limited resources to procure chemical protective clothing. These organizations often must rely on a single type of chemical protective suit to meet their chemical response needs. Users also need some level of confidence that their selected clothing will perform as intended or according to the manufacturer's claims. Furthermore, it is difficult to compare products when manufacturers report data or features of their suits differently. Even chemical data taken using the same standard test method cannot be easily be compared due to differences in reporting documentation. More importantly, however, protective clothing can be manufactured which does not provide adequate protection due to poor construction or quality assurance.

Comprehensive protective clothing standards are clearly needed. On August 12, 1983, a tank car loaded with dimethylamine located on an industrial railroad track in Benicia, California began leaking product. Firefighters, wearing chemical protective suits, responded to the leak. However, shortly after working on scene, the visors of their protective suits became cloudy and one visor eventually shattered and exposed the wearer to large concentrations of the chemical.[1] Information available to the fire department about the particular chemical protective suit led the firefighters to believe that the suits offered adequate protection for the hazardous dimethylamine environment. In investigating the accident, the United States National Transportation Safety Board (NTSB) recommended that several federal agencies work together in this area to promote consensus standards that would lead to improved products and greater confidence in using them.[2]

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* The opinions in this paper are those of the author, and do not necessarily represent the views of the U. S. Coast Guard, Amercian Society for Testing and Materials, or the National Fire Protection Association.

The U. S. Coast Guard together with the Environmental Protection Agency, Federal Emergency Management Agency, National Institute for Occupational Safety and Health Administration, and Occupational Safety and Health Administration have formed a Workgroup to comply with the NTSB recommendation. The role of this workgroup is to coordinate U. S. Federal agency research in the area of chemical protective clothing. This also involves reporting progress on Federal R&D outside the U. S. government, and actively participating in both ASTM's F23 Committee on Protective Clothing and a newly established subcommittee of the National Fire Protection Association to pursue standards for chemical protective suits.

TYPES OF STANDARDS AND STANDARDS DEVELOPMENT PHILOSOPHY

In general, there are three types of standards which can be applied to chemical protective suits: documentation, performance, and design. Documentation standards direct manufacturers to perform specific tests and to report certain data from those tests to users. These type of standards may also require manufacturers to provide information to users about their products such as a complete description of the materials used in fabricating a garment. In a performance standard, a property or characteristic of the product is measured and a required level of performance is set that the manufacturer's product must meet. For example, the garment material in a chemical protective suit might have to possess a tear resistance of at least a certain value. These standards are also called minimum performance requirements because the product must attain a minimum level of performance. The most rigorous standards are design-oriented. Design standards specify to the manufacturer the exact way a product must be constructed. These standards are generally avoided because they are design-restrictive, i.e., they do not allow manufacturers latitude to devise innovative designs for their products.

Both ASTM and NFPA appear to have distinctly different but compatible approaches in their development of protective clothing standards. The current focus of ASTM is to develop standards which measure the properties of materials used in chemical protective clothing, or establish test methods to measure the performance of complete protective garments. Already, several standards exist which specify methods for making these measurements. Moreover, standards from other ASTM committees, like those of D-11 on Rubber, can be applied to protective clothing. Therefore, ASTM's direction is one of providing performance measurement techniques which will standardize product documentation. To this end, the ASTM F23 committee has a task group working on a comprehensive documentation standard for chemical protective suits which will require manufacturers to specify certain information and conduct particular tests on their respective products.

In contrast, NFPA is working on performance standards which will set specific requirements for chemical protective suits. A Subcommittee on Hazardous Chemical Protective Clothing under NFPA's Technical Committee on Protective Equipment for Firefighters is developing several standards of this type. For these standards, manufacturers will not only have to conduct certain tests and report the results, but also meet the required minimum performance. To be compliant, a manufacturer's product must meet all requirements of the standard. As with ASTM specifications, manufacturers completely complying with a standard are able to label their product as compliant. Many standards specify the wording and type of compliance label to be issued.

CLASSIFICATION OF CHEMICAL PROTECTIVE SUITS

Several classification schemes exist for chemical protective clothing. Some are based on design while others are related to the function or application of the protective clothing. One of the better known classification systems was developed by the U. S. Environmental Protection Agency using level of protection to distinguish between types of protective clothing.[3] Four levels, A to D, were established using the degree and type of toxicity hazard to select the appropriate protective clothing, breathing apparatus, and other associated equipment. These levels and the recommended criteria for using them are listed in Figure 1. While this scheme lends itself to classifying protective clothing systems, it was not designed to categorize chemical protective suits. Certain areas are subject to interpretation. For example, it is not clear whether a Level A suit must completely enclose the user and his/her respiratory protection, or if the respiratory equipment can be worn on the outside of the suit. Additionally the selection of the garment based on its "durability" is left to the judgement of the user. These types of distinctions are essential to the development of various chemical protective clothing standards.

A classification system under consideration by the NFPA uses the EPA's Level of Protection as its basis. The highest level, Level A, dictates the use of a totally-encapsulating suit primarily in those cases where any dermal exposure to the chemical(s) is not permissible. The NFPA proposes to classify this type of clothing as "vapor-protective". Chemical protective suits recommended for both Levels B and C include one- or two-piece chemical "splash suits". The NFPA proposes to define this type of clothing as "liquid-protective". The reason for this distinction is to provide a means for verifying the performance of each protective clothing type. Therefore, classification of a chemical protective suit can be based on whether the suit can meet a performance test as opposed to its design attributes (performance-oriented versus design-oriented definition).

Another part of the proposed NFPA classification scheme would further subdivide the vapor- and liquid-protective chemical protective suits by clothing durability and function. Here the intent is to discriminate between "disposable" or "limited-use" and "rugged" protective suits. Again, the actual distinction would be based on a battery of performance tests or perhaps difference performance requirements. The end result would be a two-by-two matrix of chemical protective suits differentiated by performance. In reality, it is highly probable that each type of chemical protective suit would have a number of standard requirements in common and form the "core" requirements for each of the four chemical protective suit standards.

CHEMICAL RESISTANCE REQUIREMENTS

One of the most difficult areas in developing standards for chemical protective clothing is the measurement of clothing chemical resistance. The ASTM F23 Committee has made significant advances in establishing standard methods for measuring the permeation (ASTM F739), penetration (ASTM F903), and degradation (Draft ASTM F23.30.03) resistances for protective clothing materials. These phenomena relate to the different types of chemical interaction with the protective material and are well described elsewhere.[4,5] Measurement of permeation resistance is a likely requirement for vapor-protective clothing, where the clothing materials should prevent any intrusion of the hazardous chemical. This method can show the effects of material chemical degradation as well. Liquid-protective clothing materials, on the other hand, should be tested for penetration resistance. This distinction is important because the qualifying test for liquid-protective clothing permits vapor penetration. The ramification of this proposal is that users should only select liquid-protective clothing if exposure to vapors of the subject chemical(s) is permissible and considered non-hazardous.

Permeation Resistance Testing

Permeation resistance is the currently recommended method for measuring material chemical resistance. ASTM F739 specifies procedures for measuring permeation resistance by gases and liquids of protective clothing materials using the apparatus pictured in Figure 3. This method is the most complex of the three and its measured parameters--breakthrough time and permeation rate--are subject to variations produced by the environment, equipment, material, and testing chemical. As a consequence, results from the test are not easily compared between laboratories. Yet, a number of organizations use permeation breakthrough times as the basis for recommendations on using chemical protective suits. Also inherent is the method, is the difficulty for relating data on a pristine material to exposure conditions encountered in the field for an entire suit.

Specification of key test parameters and procedures can help further standardize the ASTM permeation resistance test. Foremost among these is the minimum detection limit of the analytical device used to detect breakthrough time. For the same material, chemical, and test conditions, a poor analytical detection limit can result in a relatively longer breakthrough time than one obtained using a very sensitive analytical technique. In some cases, the results can be rather dramatic. On a new material, the breakthrough time for carbon disulfide was reported in excess of 8 hours using flame ionization gas chromatography, whereas the same material-chemical combination with a electron capture detector yielded a breakthrough time of 30 minutes.[6] Testing laboratories cannot be expected to choose the same detection methodology for each chemical. If a minimum detection limit was set for all permeation resistance testing, then many of these disparities might be avoided.

Similarly, the configuration of the test apparatus can affect the permeation breakthrough results. Depending on the type of analytical detector chosen, systems can be either "open" or "closed". Open systems are typically used for continuous sampling of the permeation cell collection medium; closed systems for discrete sampling. In closed systems, the chemical permeant accumulates in the collection side of the permeation cell until the concentration can be detected by the analytical device. Breakthrough times measured in this way are shorter than those for open systems where there is no accumulation. It is conceivable that the rate of permeation can be so small that permeation can be detected in an closed loop system but not in the analog open configuration. However, specifying open or closed permeation system configurations would reduce the testing laboratory's flexibility in choosing analytical detectors. One way of overcoming this problem is to measure detector sensitivity independent of the permeation system configuration. Measurement of a minimum permeation rate may provide a workable approach.

The length of the test is decided by the testing laboratory but is most often related to the expected use time of the protective clothing. For chemical protective suits, testing periods range from one to eight hours. However, many suit use recommendations are based on the criterion of no breakthrough of the respective chemical within one hour. The supporting reasoning is that most users in emergency response wear a chemical protective suit for less than one hour due to the limitation of air from self-contained breathing apparatus, and the severe physiological demands imposed by wearing the suit for that length of time.[7] Some researchers believe that this one hour period includes a large safety factor because testing involves constant liquid (or gas) contact with the material over the entire test period.[8] Both the ASTM and NFPA are considering minimum test period of three hours; for NFPA, a performance requirement of one hour is being proposed.

Penetration Resistance Testing

ASTM F903 specifies the procedures for measuring the liquid chemical resistance of materials. This method involves subjecting the material to the liquid at a a specified pressure head of 2 psi (13.8kpa) and noting the time when visible penetration of the liquid occurs. In the penetration test apparatus, the clothing material acts as a partition separating the hazardous liquid chemical from the viewing side of the test cell. This apparatus is pictured in Figure 4. The ASTM method is used to identify protective clothing materials and constructions that limit the exposure to hazardous liquid chemicals. The method is not applicable for measuring vapor penetration. Significant amounts of the chemical may permeate the specimens that pass penetration tests.

Selection of Chemicals

To fully evaluate a chemical protective suit's chemical resistance, it would be necessary to conduct testing of the all suit materials for all the chemicals a response organization had the possibility of encountering. For the Coast Guard, this would amount to over 1100 chemicals listed in its Chemical Hazard Response Information System.[9] A number of these chemicals can be eliminated by taking into account their chemical state and toxicity. Yet, it is still an nearly-impossible task to test all material and chemical combinations. In order for a standard to be useful, some means of selecting priority chemicals must be adopted.

Both the ASTM and NFPA are engaged in devising standard chemical batteries for testing the chemical resistance of protective clothing materials. ASTM F1001 specifies a standard list of 15 chemicals (Table 1) which represent a wide range of chemical classes and hazards. NFPA is considering using the ASTM list with the addition of ammonia and chlorine. Requiring permeation or penetration test results on a minimum number of chemicals would allow comparison of the general chemical resistance performance between different products. However, the chemical resistance limitations of a chemical protective suit must still be determined by testing against the priority chemicals for each respective response organization.

Selection of Suit Materials

In the past, the practice has generally been to test the primary or garment material of chemical protective suits exclusively. This has resulted in suit use recommendations based on the garment material only without consideration for the other materials making up the suit. Visors, faceshields, gloves, boots, and garment material seams are exposed areas of chemical protective suits also likely to be exposed during a chemical incident. The dimethylamine spill in Benicia illustrates this point. Other major materials used in the construction of the suit or together with the suit must be evaluated in the same manner as the garment material. Thus, recommendations for using chemical protective suits must be based on the chemical resistance of all major materials with the chemical resistance of the weakest material being the limiting factor. If a breathing apparatus is worn outside the chemical protective suit, or if airline hoses are employed, the external materials of these items should be subjected to the same tests as the suit materials.

Proposed Documentation and Performance Requirements

Documentation requirements for chemical resistance testing should include either permeation or penetration testing as appropriate against a limited number of representative chemicals. Standards must go on to specify how the different tests are conducted. For example, ASTM F739 could be recommended for measuring permeation resistance with the qualification of a minimum detection limit of 1 ppm and a three hour test period for each material-chemical combination tested. These tests should be performed for every major material used in fabricating the garment including at least the garment, visor (faceshield), glove, and boot materials. The main purpose of such a documentation requirement is to allow users to compare products with the same information. This would also let users assess a chemical protective suit's ability to resist mixtures and unidentified chemicals.

Performance requirements for chemical protective suits should be chemical specific. If standards are used to support the quality of products used in chemical spill response, the chemical resistance performance requirements should reflect the needs of response organizations. Furthermore, it should be left to the users and the manufacturers to determine the chemicals for which a suit must meet the performance requirements. For these reasons, a generic performance requirement is recommended such as "no permeation breakthrough (for vapor-protective suits) or detectable penetration (for liquid-protective suits) in one hour." Like the documentation standard, the performance requirement must define the test method and parameters (i.e., minimum detection limit). In this manner, the manufacturers can logically choose which chemicals to test their products against based on expected performance and user demand. Additionally, incentive is provided to manufacturers to test as many chemicals as possible to market their products. Following this approach, the end-result will be a list of chemicals associated with each chemical protective suit with compliance based on standardized testing.

Additional chemical resistance requirements apply to other suit components which are not flat sheet materials that easily lend themselves to the above methods. These include suit seams, the suit closure, gaskets, and vent valves. Suit seams can be tested for both permeation and penetration using the standard methods above. However, special gaskets must be used with the permeation test cell to prevent leakage along the non-uniform profile of the suit seam. Suitably sized specimens and test cells must be fabricated to perform penetration testing on the suit closure. Suit gasket materials may be tested as sheet materials. As with other materials, the performance of these components should be considered in understanding the limitations of chemical protective suits. Suit seams should possess chemical resistance at least equal to the garment material itself.

To this point, all recommended testing has been proposed for virgin materials. Users need to know how the materials will perform following actual use. One way of providing an indication on how suit material chemical resistance changes with wear, is to test the materials after some form of physical abuse. Early proposals recommended creasing materials, then subjecting the creased materials to either the permeation or penetration resistance tests. More recent ideas include the use of standard material flexing devices which perform reproducible mechanical actions such as the Gelbow tester specified in U. S. Federal Standard 101C,2017. The chemical resistance performance of the flexed garment material could then be compared with pristine samples. A radical decrease in performance would indicate the high probably of material failure in the field. Crude testing of this nature has already been performed for a number of materials against methyl isocyanate. In one case, a virgin material sample demonstrated permeation resistance of 8 hours that fell to 10 minutes for samples that had been creased.[10]

PHYSICAL PROPERTY REQUIREMENTS

Both ASTM and NFPA are only in the early stages of identifying which physical properties are meaningful to users. Several standard methods for measuring material physical properties are available in the form of ASTM, NFPA, and U. S. Federal Standards. Most of these test standards involve testing particular material types (textiles, elastomers, plastics, and coated fabrics) as opposed to materials for specific applications. The difficulty in using many existing methods is relating test results to expected field conditions. For example, the way in which material tensile (or breaking) strength is measured is by noting the force required to pull the material apart in tension. This action may or may not have an equivalent phenomena in the field. Therefore, physical property test methods must be chosen which simulate the wear conditions expected by chemical protective suit users.

Efforts are underway in both ASTM and NFPA to classify physical properties in categories of material strength, integrity, and durability. One recommended battery of tests is provided in Table 2. Different materials in the chemical protective suits will have certain properties associated with the function of the material in the design of the suit, such as light transmission characteristics for suit visors. Of great concern to suit users, is the ability of protective suits to withstand field hazards such as tears, cuts, punctures, and abrasion. Material integrity may be examined by testing materials for tensile or bursting strength, and hydrostatic resistance. These same integrity tests should be applied to suit seams and closures which should demonstrate at least the same performance as the garment material. Material aging might be evaluated through methods for measuring resistance to UV light, ozone, and heat degradation. Other properties such as stiffness can be measured under varying temperature to determine low or high temperature performance. Flame resistance is another important property of concern to users.

A single method for each of the relevant properties should be identified which can accomodate the different types of materials used in chemical protective suits. Selection of a single method encourages standardization of physical property testing by manufacturers and material suppliers. It also allows users to compare material characteristics of various similar products. Nonetheless, the choice of a single method of each physical property is difficult. Chosen methods must not only allow testing of different material types (plastic film versus coated fabric), but also discriminate between the qualities of each material. For example, some protective clothing materials become stiff and brittle in cold temperatures. The application of a cold temperature bend test (ASTM D2136) shows these materials passing at -25°C. In this case, the method does not support the observed phenomena and does not discrimate material cold weather performance. However, two methods (ASTM D1043 and FED STD 191A,5202) show significant cold temperature differences in material performance and can be related to field experience.[11] Test methods can only be chosen by comparing test results for a number of different representative materials. In this manner, problems with the test method can be noted and modifications made for measuring the appropriate parameters.

The choice of performance requirements versus documentation requirements for material physical properties depends on how relevant the material characteristic is to field performance and how much the property varies among materials. Most current material physical property specifications are found in military standards for related types of clothing. The basis for many of these requirements is unclear. Minimum material performance in terms of physical properties should only be established when the material characteristic is closely related to physical phenomena that the method attempts to measure. In any case, most material physical property requirements are arbitrary. One benefit of their use is to encourage improvement of materials in terms of strength, durability, and other characteristics.

COMPONENT FUNCTION TESTS

Suit exhaust valves are used in most vapor-protective suits to allow venting of exhaust air from the self-contained breathing apparatus worn inside the suit. These valves are constructed of materials with relatively poor chemical resistance and have uncertain performance. Manufacturers employ valves with cracking pressures ranging from 0.1 to 3.0 inches water guage pressure (1.9 to 8.7 mm Hg) on totally- encapsulating chemical protective suit to maintain a small positive pressure inside the suit. It is assumed that this positive pressure prevents the diffusion of hazardous vapors into the suit via poor seams, closures, or worn material. Little testing has been conducted to determine the performance characteristics of suit exhaust valves. It is not known, for example, whether different types of valves are truly one-way, preventing negative pressures in the suits and the backflow of chemical through the valve(s), and how different operating pressures may affect this performance. Understanding the performance of these components requires that standard techniques be established. The Coast Guard is sponsoring a study to examine the performance differences between valves using a two chambered test apparatus with a breathing machine.[12] One side of the chamber acts as the outside environment with a challenge chemical while the other side represents the interior of the suit. This testing will provide the basis for both comparing and improving suit exhaust valves.

Other component functional tests may be applied to suit closures, fittings, or accessories. Suit closures like seams should offer the same protective qualities as the garment material. As previously described, closure performance can be ascertained through chemical resistance and physical integrity testing. However, this testing should also be performed after the closure has been operated several times due to wear that can change the performance characteristics of the closure. Many manufacturers employ splash covers for both suit exhaust valves and closures. These covers are either flaps of materials or inverted pockets which protect sensitive suit components from direct impingement of liquid splashes. Specification of splash covers to protective these components may be one area where design requirements are justified.

OVERALL SUIT TESTING

Only a few types of methods exist for evaluating the complete protective garment. These methods can be classified in the categories of garment pressure (inflation) testing, qualitative leak testing, and manned suit functionality testing. Variations of the methods in each category exist; some methods are more quantitative than others. Only draft standards have been proposed for garment pressure testing and qualitative leak testing. These methods are only applicable to vapor-protective clothing. There are no current tests for evaluating the integrity of liquid-protective clothing in preventing liquid penetration through the total garment. Possible tests include using chambers outfitted with nozzles to spray liquid (water) against a suit ensemble dressed on a mannequin. Penetration might be qualitatively measured by using a dye in the liquid to stain special garments worn on the mannequin underneath the suit, or water (moisture) sensors in the mannequin itself.

Garment Pressure Testing

The most widely used methods for assessing chemical protective suit integrity involve the practice of inflating the suit to determine leakage. Pressure testing measures the integrity of the suit and visor material, suit seams, and suit seams for gas-tightness. In the test, the suit is inflated to a specified pressure and either the pressure drop is measure over time, or a soap solution is applied to the outside of the suit for observing the appearance of bubbles (to detect leaks). The suit exhaust valves must be closed (or plugged) to perform the test, and a provision must be made for attaching a pressure guage. Some manufacturers specify the pressure to which the suit should be inflated. The proposed ASTM method (F23.50.01) specifies a maximum inflation pressure (3 inches water guage pressure), a test pressure (2 inches water), and an allowable pressure drop (20%) over a three minute period. It also requires using the soap solution to locate leaks if the suit does not meet the pass/fail criteria. The method is illustrated in Figure 5 and appears very sensitive to small leaks in the garment. Tests with representative suits show that suits failing the ASTM pressure test give high protection factors from qualitative leak testing described below.[13] Pressure testing is well suited as a performance requirement for individual suit quality assurance by manufacturers.

Qualitative Leak Testing

Qualitative leak testing measures the integrity of the entire chemical protective suit to a gaseous or aerosal challenge agent in a manner simulating actual use. This testing involves the exposure of a test subject wearing the suit and a self-contained breathing apparatus in a closed chamber, and measuring the gas challenge agent concentration both inside and outside the suit. The proposed ASTM method (F23.50.02) employes ammonia gas at a concentration of 1000 to 2000 ppm and length of stain detection tubes. The test subject also engaged in a series of exercises to test the suit under dynamic conditions. This test was principally designed as a field test and would be difficult to use in manufacturing quality control because of its qualitative nature.

Other variations of this method may use different gases or aerosols (at non-toxic concentrations) and the appropriate methods. Dependent on the means used to measure the concentration of the gas, the test can be qualitative, semi-quantitative, or quantitative. When the concentration methods are both precise and extend over a large detection range, the results can be used in a semi-qualitative manner by ratioing the external to internal challenge agent concentrations to calculate a "protection factor". Large protection factors are indicative of high suit integrity. The measurement of protection factors is a widely used practice for assessing breathing device integrity. During these tests suit pressure can also be monitored to determine if relative pressures become negative to allow penetration of the challenge agent.

Manned Functionality Testing

Manned suit testing is often performed to determine the range of activities that a user can do while wearing the chemical protective suit and a breathing apparatus. These may include different types of exercises or task which simulate the end application of the chemical protective suit. Results from these tests are generally subjective regarding the design, comfort, and fit of the garment. Measurement of the wearer's physiological condition (e.g., core temperature, skin temperature, heart rate, and blood pressure) during this testing serve as a means for quantifying the physical stress on the wearer when compared to the same tests of the subject not wearing the suit. One study of this type had already demonstrated significant physiological differences for the wearing of different chemical protective suits.[14] Because these tests are subjective and not reproducible, they are not appropriate for manufacturing performance standards. Nevertheless, this testing is ideal for user acceptance testing or evaluations to compare different products.

CONCLUSIONS

Once these standards are developed, protective clothing users will be able to examine a garment for compliance labels and know if the garment meets the minimum requirements of either ASTM or NFPA. The ASTM documentation standard will allow a user to compare chemical protective suits with the same information from product to product. The NFPA minimum performance standard would provide a suit user with some confidence that product "passes" specific tests to provide a minimum level of performance. Collectively, the standards should provide incentives to manufacturers to improve their products and allow a framework within the marketplace to encourage competition.

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TABLE 1. Standard Chemicals for Evaluating Protective Clothing Materials[a]

Chemical	Chemical Class
Acetone	Ketone
Acetonitrile	Nitrile
Carbon Disulfide	Sulfur Organic Compound
Dichloromethane	Chlorinated Hydrocarbon
Diethyl Amine	Amine
Dimethylformamide	Amide
Ethyl Acetate	Ester
Hexane	Aliphatic Hydrocarbon
Methanol	Alcohol
Nitrobenzene	Niitrogen Organic Compound
Sodium Hydroxide (50%)	Inorganic Base
Sulfuric Acid (93.1%)	Inorganic Acid
Tetrachloroethylene	Chlorinated Hydrocarbon (Olefin)
Tetrahydrofuran	Heterocyclic Ether
Toluene	Aromatic Hydrocarbon

[a] These chemicals are recommended in ASTM F1001, "Standard Guide for Test Chemicals to Evaluate Protective Clothing Materials".

TABLE 2. Recommended Battery of Physical Property Tests for Chemical Protective Suit Materials[a]

GARMENT MATERIAL

Physical Property	Test Method
Abrasion Resistance	ASTM D3386
Bursting Strength*	ASTM D3786
Cut Resistance	ASTM F23.20.01 (draft)
Flammability	ASTM D568
Flexural Fatigue	FED STD 101C,2017
Hydrostatic Resistance	ASTM D751
Puncture Resistance	ASTM F23.20.02 (draft)
Stiffness (with temperature dependence)	ASTM D1043
Tear Strength	ASTM D751
Tensile Strength*	ASTM D751

VISOR MATERIAL

Physical Property	Test Method
Distortion	ASTM D881
Impact Strength	ASTM D3029
Light Transmission and Haze	ASTM D1003
Scratch Resistance	ASTM F548

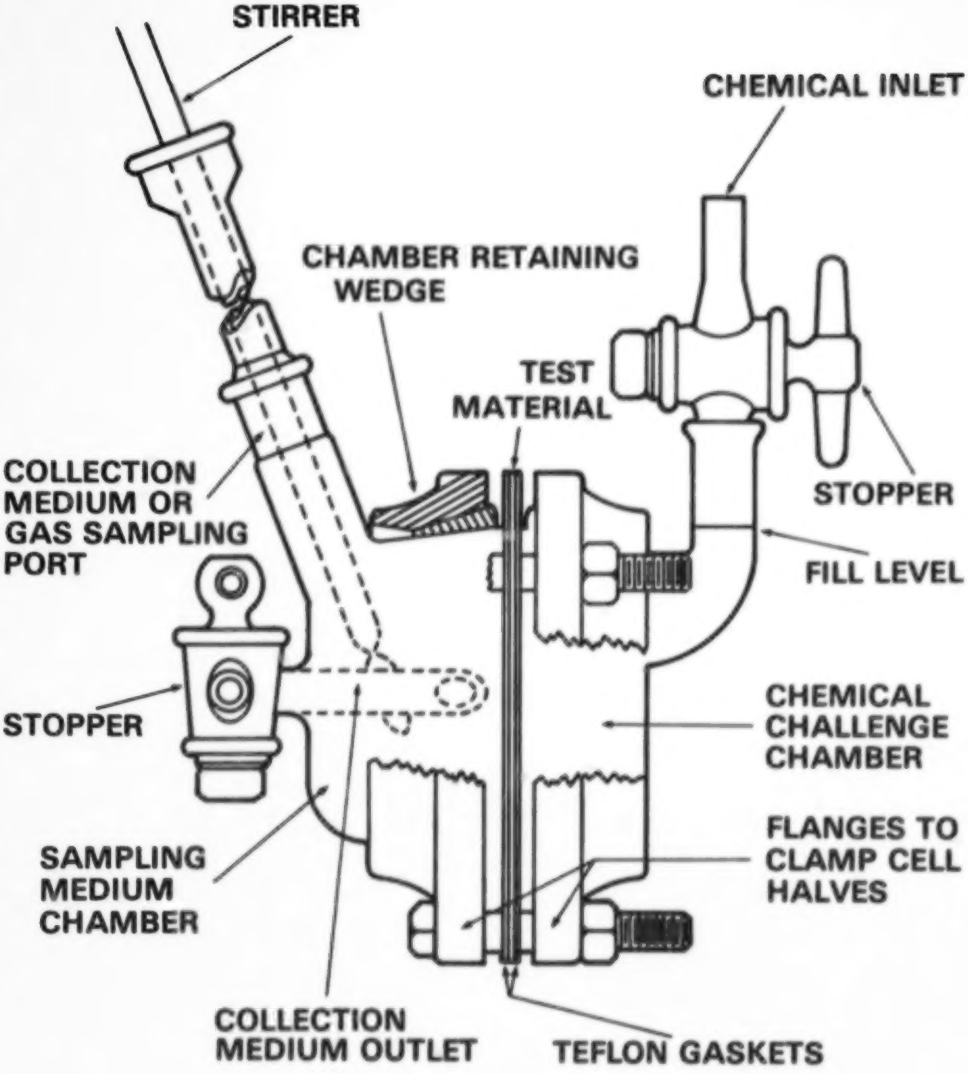
* These tests can also be used to determine the strength of suit seams and closures.

[a] These properties are recommended in reference

LEVEL OF PROTECTION	EQUIPMENT	PROTECTION PROVIDED	SHOULD BE USED WHEN:	LIMITING CRITERIA
A	RECOMMENDED: • Pressure-demand, full-facepiece SCBA or pressure-demand supplied-air respirator with escape SCBA. • Fully-encapsulating, chemical-resistant suit. • Inner chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Two-way radio communications. OPTIONAL: • Cooling unit. • Coveralls. • Long cotton underwear. • Hard hat. • Disposable gloves and boot covers.	The highest available level of respiratory, skin, and eye protection.	• The chemical substance has been identified and requires the highest level of protection for skin, eyes, and the respiratory system based on either: – measured (or potential for) high concentration of atmospheric vapors, gases, or particulates or – site operations and work functions involving a high potential for splash, immersion, or exposure to unexpected vapors, gases, or particulates of materials that are harmful to skin or capable of being absorbed through the intact skin. • Substances with a high degree of hazard to the skin are known or suspected to be present, and skin contact is possible. • Operations must be conducted in confined, poorly ventilated areas until the absence of conditions requiring Level A protection is determined.	• Fully-encapsulating suit material must be compatible with the substances involved.
B	RECOMMENDED: • Pressure-demand, full-facepiece SCBA or pressure-demand supplied-air respirator with escape SCBA. • Chemical-resistant clothing (overalls and long-sleeved jacket; hooded, one- or two-piece chemical splash suit; disposable chemical-resistant one-piece suit). • Inner and outer chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Hard hat. • Two-way radio communications. OPTIONAL: • Coveralls. • Disposable boot covers. • Face shield. • Long cotton underwear.	The same level of respiratory protection but less skin protection than Level A. It is the minimum level recommended for initial site entries until the hazards have been further identified.	• The type and atmospheric concentration of substances have been identified and require a high level of respiratory protection, but less skin protection. This involves atmospheres: – with IDLH concentrations of specific substances that do not represent a severe skin hazard; or – that do not meet the criteria for use of air-purifying respirators. • Atmosphere contains less than 19.5 percent oxygen. • Presence of incompletely identified vapors or gases is indicated by direct-reading organic vapor detection instrument, but vapors and gases are not suspected of containing high levels of chemicals harmful to skin or capable of being absorbed through the intact skin.	• Use only when the vapor or gases present are not suspected of containing high concentrations of chemicals that are harmful to skin or capable of being absorbed through the intact skin. • Use only when it is highly unlikely that the work being done will generate either high concentrations of vapors, gases, or particulates or splashes of material that will affect exposed skin.
C	RECOMMENDED: • Full-facepiece, air-purifying, canister-equipped respirator. • Chemical-resistant clothing (overalls and long-sleeved jacket; hooded, one- or two-piece chemical splash suit; disposable chemical-resistant one-piece suit). • Inner and outer chemical-resistant gloves. • Chemical-resistant safety boots/shoes. • Hard hat. • Two-way radio communications. OPTIONAL: • Coveralls. • Disposable boot covers. • Face shield. • Escape mask. • Long cotton underwear.	The same level of skin protection as Level B, but a lower level of respiratory protection.	• The atmospheric contaminants, liquid splashes, or other direct contact will not adversely affect any exposed skin. • The types of air contaminants have been identified, concentrations measured, and a canister is available that can remove the contaminant. • All criteria for the use of air-purifying respirators are met.	• Atmospheric concentration of chemicals must not exceed IDLH levels. • The atmosphere must contain at least 19.5 percent oxygen.
D	RECOMMENDED: • Coveralls. • Safety boots/shoes. • Safety glasses or chemical splash goggles. • Hard hat. OPTIONAL: • Gloves. • Escape mask. • Face shield.	No respiratory protection. Minimal skin protection.	• The atmosphere contains no known hazard. • Work functions preclude splashes, immersion, or the potential for unexpected inhalation of or contact with hazardous levels of any chemicals.	• This level should not be worn in the Exclusion Zone. • The atmosphere must contain at least 19.5 percent oxygen.

*Based on EPA protective ensembles.

Figure 1. U. S. EPA Levels of Protection


STIRRER
CHEMICAL INLET
CHAMBER RETAINING WEDGE
TEST MATERIAL
STOPPER
COLLECTION MEDIUM OR GAS SAMPLING PORT
FILL LEVEL
STOPPER
CHEMICAL CHALLENGE CHAMBER
FLANGES TO CLAMP CELL HALVES
SAMPLING MEDIUM CHAMBER
COLLECTION MEDIUM OUTLET
TEFLON GASKETS

PERMEATION TEST CELL

Figure 2

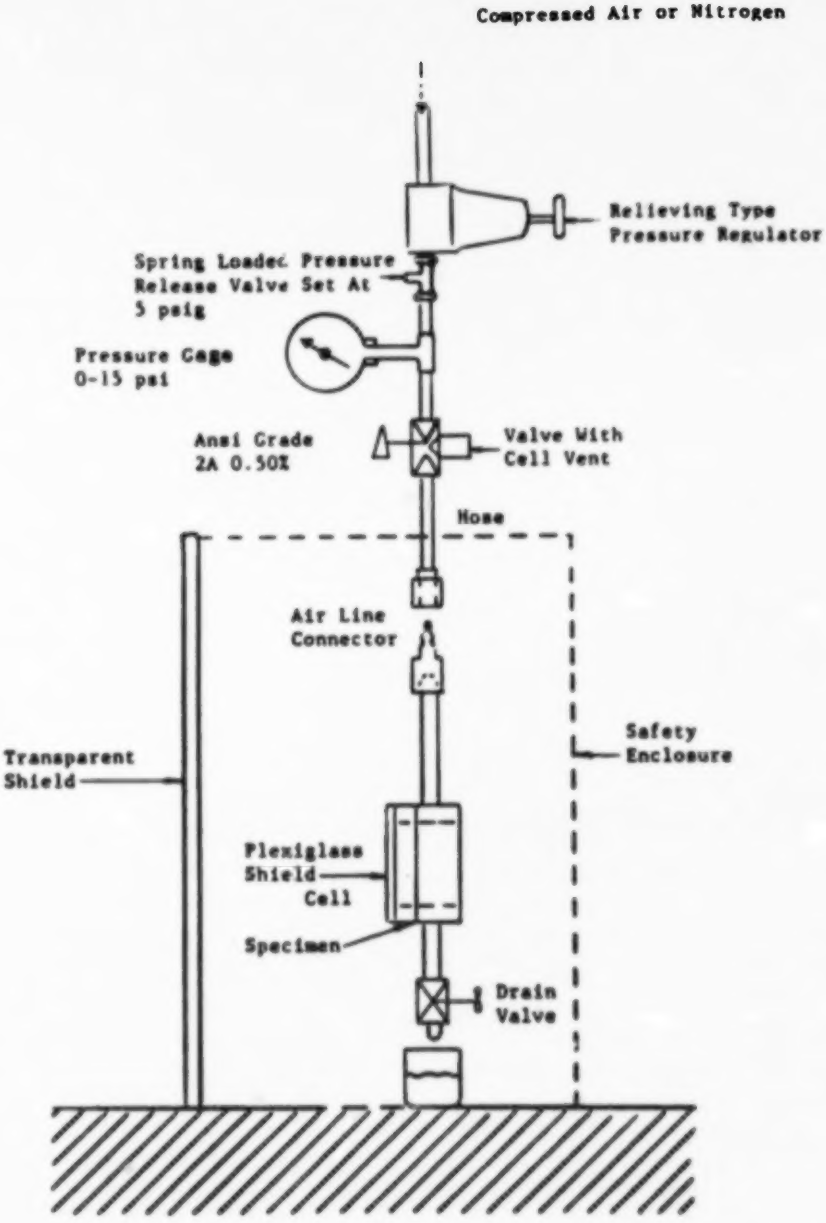

Compressed Air or Nitrogen
Relieving Type Pressure Regulator
Spring Loaded Pressure Release Valve Set At 5 psig
Pressure Gage 0-15 psi
Ansi Grade 2A 0.50%
Valve With Cell Vent
Hose
Air Line Connector
Transparent Shield
Safety Enclosure
Plexiglass Shield Cell
Specimen
Drain Valve

Figure 3. Penetration Resistance Test Apparatus

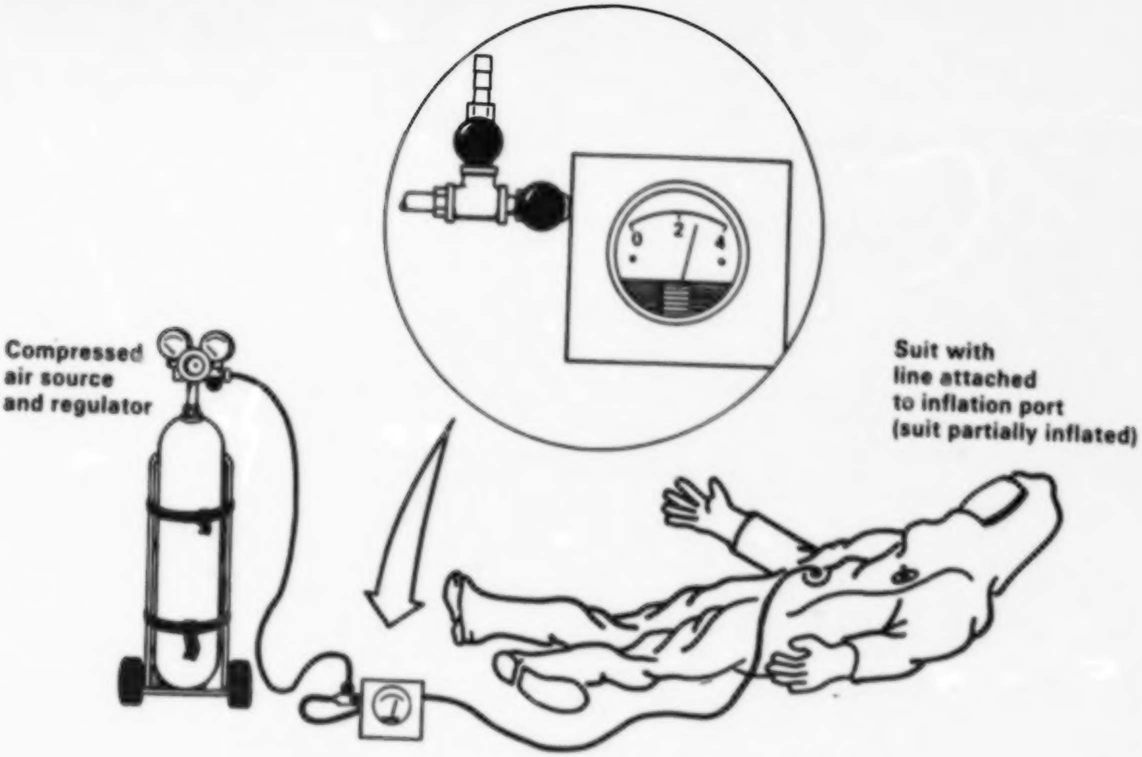

0
2
4
Compressed air source and regulator
Suit with line attached to inflation port (suit partially inflated)

Figure 4 — Recommended pressure test apparatus and typical test configuration

HAZARDOUS MATERIALS IDENTIFICATION
A QUICK FIELD IDENTIFICATION OF UNKNOWN MATERIALS

Robert Turkington
California Division of Occupational Safety and Health
San Francisco, California

ABSTRACT

The HazCat system uses forty-four one or two step field tests arranged into a decision tree format which allows a non-chemist to quickly key out an unknown material at the scene of an incident. With a few exceptions, the entire system is made up of equipment and reagents which can be stored for over a year in the trunk of a car and be immediately available for use.

BACKGROUND

California's Division of Occupational Safety and Health conducted a three-year study to look at the risk to emergency responders from exposure during fires and chemical spills. Hazardous Materials Identification was devised to provide for quick decisions on the part of Cal/OSHA Personnel who would be required to respond during the period of the study. This ability was deemed necessary after an ardous twelve hours on the San Francisco Bay Bridge which had been closed for a spill of unknown material (later determined to be talc). Initially, Hazardous Materials identification provided only enough information to stabilize a situation.

Other public agencies requested and were given training in the procedure. The training created a need for more refined tables as the users were made up of a broader spectrum of persons having varying degrees of chemical knowledge.

The number of requests increased until the class was being taught three times per week. Cal/OSHA recognized that there was a need for this type of training and decided to formalize the system. Formalization began by taking the list of one hundred and sixty of the most commonly spilled chemicals in the state of California, derived from the risk assessment study, and expanding the charts to include all of these for specific identification. Extremely hazardous materials not on the list but which could be a major hazard to a person using the system were added at this time. During this stage of development, each class was used as a research project. Students were encouraged to bring in unkowns that they had encountered. This provided Cal/OSHA a mechanism to test the validity of the system; it also tended to expand the charts quickly. Fine tuning of the system was done by modification based on student difficulty in reading the charts or performing the tests. Unknowns used in class instruction were constantly changed to ensure that all the theoretical pathways were attempted by persons new to the system. Questions from persons using HazCat in the field also resulted in numerous modifications. The charts as they are now presented are the end products of thousands of hours of hands-on testing by fire, police, health, and other response persons.

METHODOLOGY

Hazardous Materials Identification uses three tests to quickly separate an unknown liquid or solid into a unique universe. Two of these tests, the Water Solubility and Char tests are the key as they each divide materials into as many as one hundred distinct universes. After a mater-ial has passed through these two tests, it falls into an area where there remain very few possible candidates from among the more commonly encountered spilled materials. Once a mater-ial is in this realm, the devisive process is replaced by a searching process using positive identification methods to look look for common materials.

The third test is the Oxidizer test. Although this test defines only two possible universes, it quickly separates out some of the more hazardous materials. The oxidizer test is first.

The Oxidizer Test

The HazCat system uses potassium iodide paper. this test does not identify benzyol peroxide or nitrates. These are identified further into the system. This test is the first performed for two reasons: a. It is the first time an unknown is challenged with water. this challenge is perform-ed by moistening the potassium iodide paper with weak hydro-chloric acid and touching the unknown material, which is on an open flat watch dish. Even if the user was able to get sodium metal or other strong reactor to this point, the reaction would not harm the person performing the test. b. Oxidizers come in many chemical forms, and all are incompatible with other mater-ials. Since these very hazardous materials may not have many warning properties, it is best to know as soon as possible what has been spilled.

The Water Solubility Test

A small amount of the unknown is added to 10 ml of water is a test tube. There are more than 14 possible reactions when a material is placed in water. When this is considered in context with the more than 10 recongizable forms the unknown may take (e.g., viscosity for liquids, crystalline, metallic, waxy, etc., for solids), this test can separate unknowns into more than 100 unique universes. Many of these the layman is already familiar with from life experience. An example:

> Solvent-like material (no more viscous than water, but, has odor, separates from water, and/or is flammable) is placed in water; if it:
>
> a. Floats: it is most likely a petroleum hydrocarbon; secondary possiblities, plant distillate (turps) or long chain alcohols.
>
> b. Sinks: it is most likely a chlorinated cleaning solvent; secondary possibilities, freons and carbon disulfide. Hazards: more toxic than petroleum hydrocarbons; many have few warning properties; many are asphyxiants. If fire, the gases evolved may be very hazardous.

c. Dissolves: it is most likely an alcohol or acetone. Secondary possibilities, nitriles, short chain amines. Hazard: flammable. A slight possibility that the gases in a fire might be extremely toxic.

d. Emulsifies: it is most likely a pesticide, either chlorinated, thionated or organophosphate. Hazard: skin contact, extreme environmental hazard if the pesticide is chlorinated.

e. Reacts: most likely thynolchloride (commonly found in drug laboratories). Hazards: skin contact, may be explosive in many circumstances, is water reactive, probably acidic, and off-gasing material is also hazardous.

Oily material (viscous) is placed in water; if it:

a. Floats: it is most likely a petroleum hydrocarbon or plant distillate, also possibility of cooking (plant or animal oil). Hazard: flammable to combustible, depending upon how viscous the material appears (how it coats the side of the test tube). Primary concern--is this a carrier for some other product, PCBs, etc.?

b. Sinks: this is an area where some of the most hazardous materials are found; therefore, with oily things that sink, Hazardous Materials Identifications becomes very conservative. The most common spill is PCB which is the most likely candidate and therefore, the first thing that the system at looks for. If this is ruled out, then one has to consider the possibility of such chemicals as organometals and aniline. Hazard: if not PCBs, may be extreme skin contact poisons. Fire may produce extremely hazardous gases.

c. Dissolves: most likely, sugar solutions, or soap, however, one must consider long chain amines. Hazard: if the material has a very high pH, you may have an amine; these can be very hazardous both upon skin contact, and by inhalation. Sugar solutions, if found under suspicious circumstances, should be considered as possible baits.

d. Emulsifies: if very viscous, you may have a cutting oil, but before you can classify as such, you must rule out pesticides.

This process continues for liquids including pastes, goos, aqueous solutions and gels.

The Char Test

Take about 10 ml of the material, place it in a test tube and heat using a propane torch, continue to heat until no further change takes place in the material being heated. For safety's sake, in Hazardous Materials Identification the Char Test has been broken into 3 tests. One has only to consider the results of placing 10 ml of a flammable liquid into a test tube and heating it to 1800· to understand. The second manifestation of the char test is called the Combustibility test. In this test, a small amount of a liquid is placed into a color plate, and a match is touched to the surface, if it is impossible to get the material to burn, then the more traditional char test may be done. The third test, Ignition, is unique in that it allows the person doing the test to use his/her creativity, to ignite the material any way they feel is possible. This test picks up such diverse materials as sulfur, magnesium, acetylene and hydrogen gases, and polyol solutions. The char test gives over 12 possible results, and in conjuction with the combustibility and ignition tests give 15 exclusive results placing the user into numerous possible universes. Initially the char test was the primary test, however for the sake of safety it was relegated to the secondary divisive test, where it is used mainly to distin-guish between organic and inorganic materials. The char test far more than the water solubility test gives very specific indications of what the unknown might be. In general, it identifies salts, oxides, silicates, and mixtures; more specifically, it identifies nitrates, ammonium salts, and arsenic salts.

Since so many hours of hands on time has been devoted to this system, and the changes since conception have been so great, by the time that a person arrives at the positive confirmation tests, the potential interferences have been largely eliminated. Highly technical persons may feel a faster method is available, as they pass through the series of tests, but the screening tests, and safety loops are based not upon the easiest method for achieving identification, but elimination of confusion and false positives for the uninitiated user.

Perhaps the most unique of these screening tests is the hexane/alcohol solubility test with its ability to pick out solid poisons such as pentachlorophenol, and parathion before these can get into the body of the system. Although these would eventually be found, this greatly shortcuts the process, and excludes many confusing results in the down stream positive tests.

Hazardous Materials Identification will not stop at a first identification or a Hazard category. Often it will force a user through two or three categories, before describing the material as; a water reactive acid, flammable peroxide, or carcin-ogenic oxidizer.

When a positive identification is finally made, previous tests become part of the confirmation. An example: The final test in the series keying out organophosphates uses the technique of killing cholinesterase enzymes. Prior to that final test, the user will have passed through the following observations:

1. Foul odor; 2. Emulsified in water; 3. pH was slightly acid; and 4. A confirmation of phosphate ion. If a person wishes to go further he can dd sodium hypochlorite. If it turns red, the unknown is methylparathion one of the more toxic of the organophospates commonly available.

If after all tests, the screening and safety loops the mater-ial is still unidentified, the user will still know the following:

a. Is the unknown material organic or inorganic? It is here that the Char test may be the most useful, in that, if the unknown is not volatile or reactive at 1800·, although it may remain an unknown, the responder can make the assumption that the material is not likely to be airborne and clean it up using the criteria for cyanide.

b. The hazard category into which the material falls, (with the exception of toxic, which is always a good assumption).

An example: A fire department keyed out a material as unknown. By testing they knew it was aromatic, chlorinated, flammable, and acidic. When a laboratory analysis was finally available, the material turned out to be a mixture of toluene, perchloroethylene, and formic acid. Although not specifically identified, the fire fighters knew how to handle the liquid.

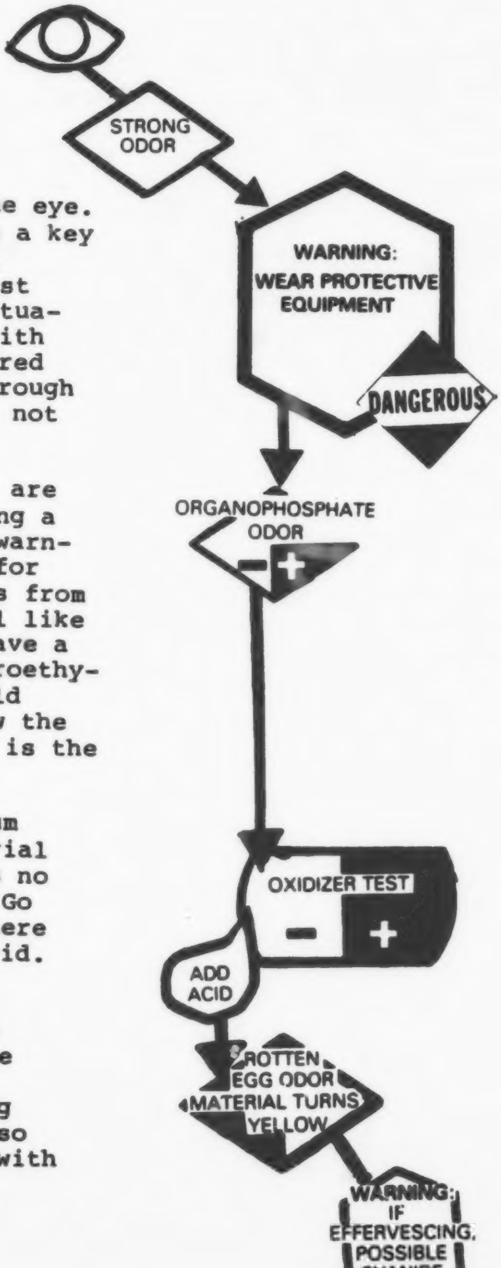
The Hazardous Materials identification system incorporates 5 colorimetric paper strips, 7 dreager tubes, the EPA Asbestos ID system, Enztec organophosphate test strips, the Chlor-n-oil test kit for PCBs, and salt solutions reagents, and specific indicater dyes. Except for some of the Dreager tubes, the reagents are very specific indicater dyes described in Fygle. Except for some of the Dreager tubes, the reagents are very stable.

The following example will show how the system works.

KEYING OUT PERCHLOROETHYLENE

An Example

KEYING OUT PERCHLOROETHYLENE USING HAZCAT


STRONG ODOR
WARNING: WEAR PROTECTIVE EQUIPMENT
DANGEROUS
ORGANOPHOSPHATE ODOR
−
+
OXIDIZER TEST
−
+
ADD ACID
ROTTEN EGG ODOR
MATERIAL TURNS YELLOW
WARNING: IF EFFERVESCING, POSSIBLE CYANIDE

Start at the eye.

Only look at the arrows leaving the eye. The arrows coming into the eye are a key to describe the meaning of arrows. There are five choices, and you must pick the choice which fits your situation. In this case, you will go with strong odor. (Any odor is considered strong.) This choice leads you through a warning sign. A warning sign is not a decision point.

If you can smell the material, you are breathing it. You should be wearing a respirator. You pass through the warning sign to a diamond (the symbol for observation). You have two choices from this point, does the material smell like a pesticide, or not? Pesticides have a remarkably bad odor, while perchloroethylene does not, therefore, you should choose the negative side and follow the arrows to the OXIDIZER TEST. This is the test you will do.

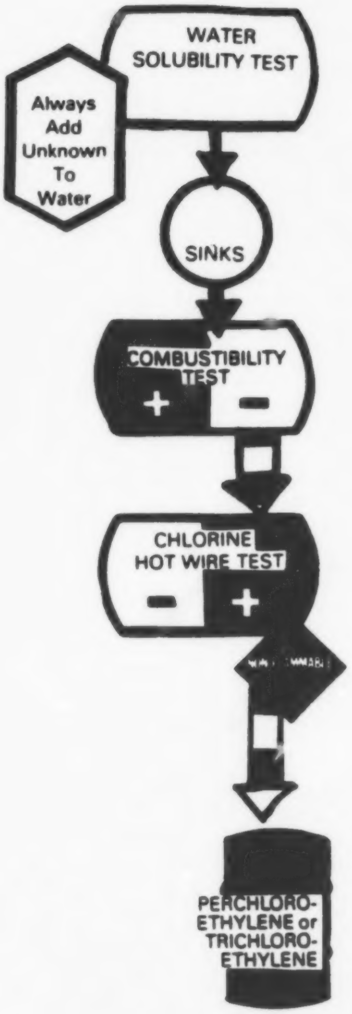
Place a drop of HCl on the potassium iodide paper, touch it to the material which is in a watch dish. There is no change in the color of the paper. Go to the negative side of the test where you see a drop. Add hydrocloric acid.

Since you are still wearing your respirator, you will not be able to smell anything now, so set aside the watch dish and go through the next observation sign, to another warning symbol. There is no effervescing, so you can continue past this warning with little notice.

Go to the WATER SOLUBILITY TEST. Place a few drops of the unknown into a test tube filled with water and observing what happens. You have eight choices - the perchloroethylene will sink. You follow that arrow to the COMBUSTIBILITY TEST. Here you have two choices, either the material burns or it will not. Perchloroethylene will not burn, so you follow the solvent arrow on the non-flammable side. Note that in this case everything except pastes, goos and gels go to the CHLORINE HOT WIRE TEST.

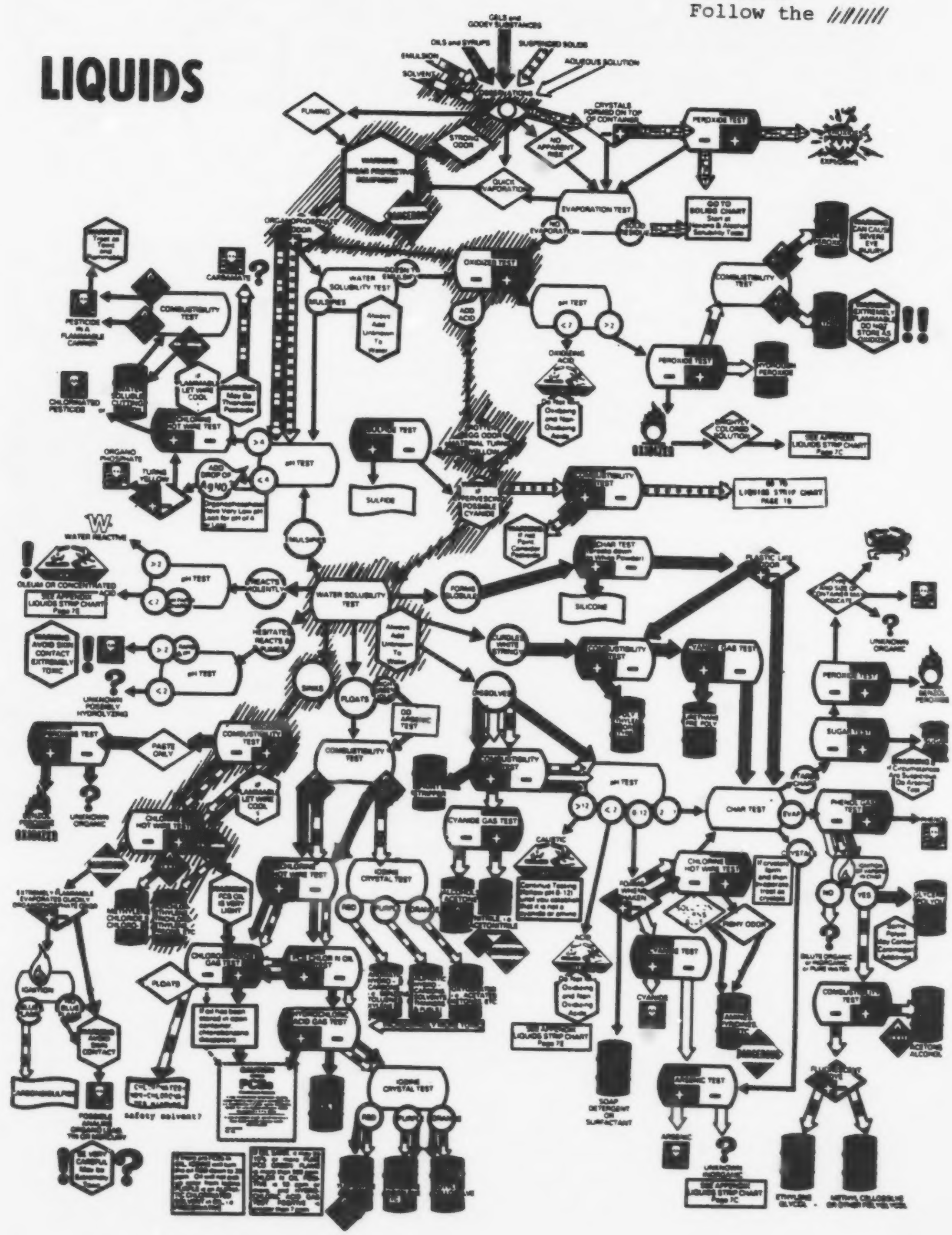
The CHLORINE HOT WIRE TEST is done by heating a copper wire to be sure that there is no residual green flame. Then place the wire into the solution and let it cool. Then reheat the wire to see if a green flame is given off. Since perchloroethylene will have a positive green wire flame, you follow the solvent arrow to perchloroethylene, trichloroethane, etc. You can further separate these by other methods, i.e., perchloroethylene will turn iodine crystals red, while trichloroethane and carbon tetrachloride will turn them purple. Freons have almost no odor, while perchloroethylene and trichloroethylene have an odor like dry cleaning fluids.

Although you may not know exactly what you have, you do know its toxic properties, and the methods for handling this material.


WATER SOLUBILITY TEST
Always Add Unknown To Water
SINKS
COMBUSTIBILITY TEST
+
−
CHLORINE HOT WIRE TEST
−
+
PERCHLORO-ETHYLENE or TRICHLORO-ETHYLENE

AN EXAMPLE
KEYING OUT PERCHLORO-
ETHYLENE
Follow the //////

LIQUIDS


OILS and GOOEY SUBSTANCES
OILS and SYRUPS
SUSPENDED SOLIDS
EMULSION
SOLVENT
AQUEOUS SOLUTION
CRYSTALS FORMED ON TOP OF CONTAINER
FUMING
STRONG ODOR
NO APPARENT RISK
PEROXIDE TEST
EXPLOSIVE
QUICK EVAPORATION
EVAPORATION TEST
NO EVAPORATION
GO TO SOLIDS CHART
OXIDIZER TEST
WATER SOLUBILITY TEST
COMBUSTIBILITY TEST
pH TEST
PESTICIDE
CHLORINATED PESTICIDE
ORGANO PHOSPHATE
SULFIDE TEST
SULFIDE
HYDROGEN PEROXIDE
SEE APPENDIX LIQUIDS STRIP CHART
WATER REACTIVE
OLEUM OR CONCENTRATED ACID
CHAR TEST
FORMS GLOBULE
SILICONE
PLASTIC LIKE ODOR
UNKNOWN ORGANIC
SINKS
FLOATS
DISSOLVES
CYANIDE GAS TEST
SUGAR TEST
BENZOYL PEROXIDE
PHENOL GAS TEST
CHLORINE HOT WIRE TEST
IODINE CRYSTAL TEST
CYANIDE
ARSENIC TEST
ARSENIC
SOAP DETERGENT OR SURFACTANT
UNKNOWN INORGANIC
ACETONE ALCOHOL
ETHYLENE GLYCOL
METHYL CELLOSOLVE OR OTHER POLYGLYCOL
safety solvent?

CONCLUSION

Using a list of commonly spilled and encountered materials, familiarity with and knowledge of industrial and household chemicals, simple tests to define these materials, time to experiment with proposed materials identification pathways both in the lab and in the classroom, has provided a tool which has been invaluable to not only the emergency responder, but forensics lab, water labs, hazardous waste haulers and a multitude of persons who need to have enough information about a material to immediately to take an action. Hazardous Material identification was never designed to preclude the use of the laboratory, but to provide the for initial screening to take some type of mitigation or containment action.

THE CONTINUING DEVELOPMENT OF A PERSON PORTABLE ANALYTICAL SYSTEM.

J.T. Ruttan
CounterSpil Research Inc.
Vancouver, British Columbia.

A.M. Bobra
Environment Canada
Ottawa, Ontario.

Introduction

Under the mandate for coordinating the Canadian federal response to spills of hazardous materials in the environment, Environment Canada initiated the Chemical Hazards Emergency Countermeasures (CHEC) Program in 1980 (Fingas, 1982). One component of the CHEC program is hazard level monitoring. Emphasis is placed on developing those analytical systems capable of rapid identification, quantification, and/or monitoring in-situ levels of spilled hazardous materials in any or all of the three environmental compartments (e.g. soil, water and air).

Analytical systems presently being developed for spill response by the Environmental Emergencies Technology Division (EETD) of Environment Canada are grouped into five categories, characterized by their portability, accuracy, complexity and capability to detect hazardous materials from Environment Canada's spills priority list. Environment Canada's designation of analytical system levels are as follows: Level I - pocket-portable, Level II - person-portable, Level III - vehicle-portable, Level IV - mobile laboratory, Level V - fixed laboratory.

This paper deals solely with the continuing development of the Level II analytical system. Information on the other systems may be found elsewhere (Bobra, 1986; Colford Townshend, 1986; Fingas, 1985; Lockwood and Halman, 1983; Dick et al., 1983).

LEVEL II ANALYTICAL SYSTEM

Instruments

The person-portable analytical system consists of three instruments intended for use at spill sites where the identity of the hazardous material is known. These instruments are effective in spill response for measuring an ambient concentration, determining the gross extent of contamination, identifying contaminant plumes and implementing effective countermeasures (Bobra, 1986). The instruments chosen by Environment Canada for the Level II system are the Century Systems Corporation Model 128 Organic Vapour Analyser (OVA), the HNU Systems Incorporated Model PI-101 Photoionization Analyser (HNU), and the Hach Company Direct Reading Engineer's Laboratory Model DR-EL/4 (Hach kit).

The OVA and the HNU instruments are used for air monitoring. Both are non-specific in regard to measuring a certain chemical out of a mixture of several chemicals. This is not a drawback, for in most spill situations only one substance is involved and it may be identified by shipping labels or waybills; moreover, the concentration of that substance is usually far greater than that of the ambient background.

Various contractors for EETD have completed a series of calibration experiments with the OVA and HNU for gases and vapours from Environment Canada's spills priority list (Dick et al., 1983; Underdown et al., 1985). Response data for a total of 48 compounds on the OVA, and 39 compounds on the HNU were obtained (Bobra, 1986). The majority of the compounds tested were pure substances although a few commercial mixtures were also tested. Conversion of the OVA and HNU calibration data into a form usable by a spill responder resulted in individual compound-specific meterscale overlays being developed for each instrument (Underdown, 1985).

The third instrument included in the Level II system is the Hach kit. Its intended use is for the analysis of contaminated soil and water systems. It is a portable laboratory containing a spectrophotometer, pH meter, conductivity meter, digital titrator, basic glassware, and pre-packaged reagents. Also included in the kit is a well written and comprehensive manual. The Hach kit is capable of detecting, in water, all of the inorganic chemicals from Environment Canada's spills priority list except hydrogen peroxide and titanium dioxide.

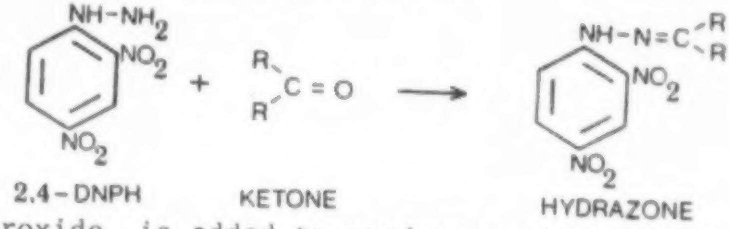
Hach Kit Modifications

Various contractors for EETD have further developed the kit for the analysis of organic and inorganic compounds in soil and water (Dick et al., 1982; Townshend Colford, 1986; Ruttan, 1986). Work on modifying the Hach kit has focused on developing procedures, and methodologies for the analysis of spill priority chemicals in soil and water. Initially, an extensive literature search was conducted, and compound specific tests were located and evaluated in regard to the Level II concept of portability. Those methods that passed preliminary evaluations were tested, and/or modified for inclusion into the Hach kit. Test criteria for acceptance included accuracy, reproducibility, sensitivity, absence of interferences, range of detection, and field portability. Presently, analytical techniques being used in conjunction with the Hach kit are either colorimetric or titrimetric methods.

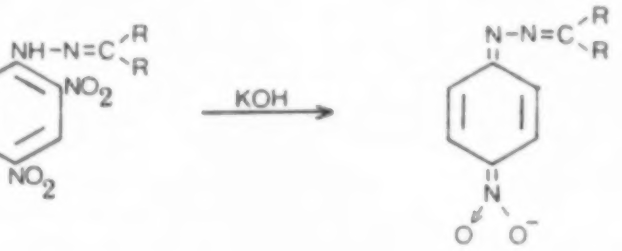
Colorimetric Methods

The existing Hach kit employs a large number of colorimetric tests for the analysis of specific compounds in water. Calibrated meterscale overlays are used in conjunction with each specific test. These overlays eliminate the need to prepare standards when calibrating the spectrophotometer for specific tests and provides an investigator with direct concentration readings. Developing such overlays for new methods was an objective of the testing phase of this project.

The 2,4-Dinitrophenylhydrazine (2,4-DNPH) test is an example of a colorimetric method used in the modified kit. This test is capable of detecting three ketones (acetone, methyl ethyl ketone and methyl isobutyl ketone) and three aldehydes (formaldehyde, n-butyraldehyde and iso-butyraldehyde) from Environment Canada's spills list. The reaction principle is illustrated below.


NH-NH2
NO2
NO2
+
R
C = O
R
NH-N=C
R
R
NO2
NO2
2,4 - DNPH
KETONE
HYDRAZONE

Potassium hydroxide is added to produce a wine-red color, presumably due to a resonating quinodal ion (Kritchfield, 1963).


NH-N=C
R
R
NO2
NO2
KOH
N-N=C
R
R
N
O
O-

The intensity of the color is then measured by the Hach kit spectrophotometer at 480 nm.

Repetitive testing and calibration of individual compound concentrations against the spectrophotometer readings enabled the investigator to convert test data into a form usable by the spill responder. Figure 1 is an example of the meterscale overlay for the 2,4-Dinitrophenylhydrazine test for Acetone in water.

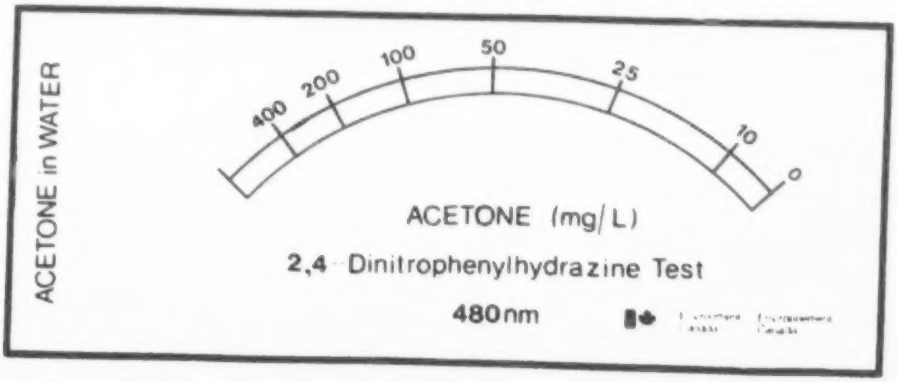

ACETONE in WATER
400
200
100
50
25
10
0
ACETONE (mg/L)
2,4 Dinitrophenylhydrazine Test
480nm

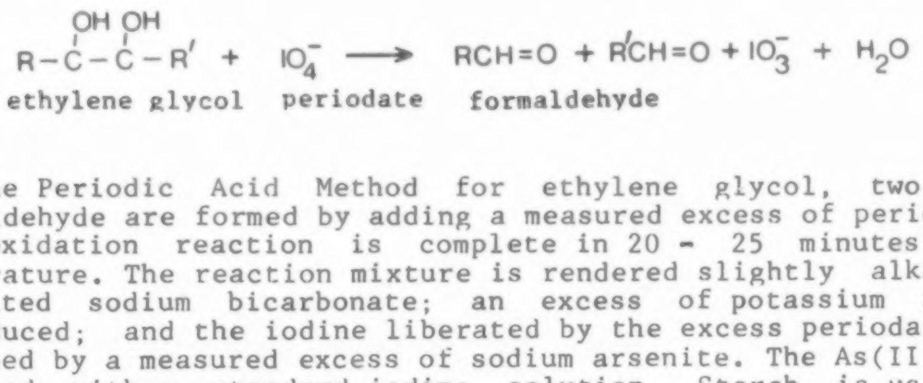
Figure 1. Meterscale Overlay for Acetone in Water.

Thus, by using the appropriate colorimetric test and meterscale overlay, contaminant concentrations can be read directly off the spectrophotometer in units of mg/L for water, and mg/kg for soil. Listed in Table 1 is a compilation of colorimetric methods which have been tested and evaluated, and have met specific test criteria for use in the Level II analytical system.

Titrimetric Methods

The existing Hach kit also employs a large number of titrimetric methods for the analysis of specific compounds. By adding variable amounts of titrant to the contaminated sample a specific color change occurs signifying an endpoint. Contaminant concentrations are determined through simple equations, calibration tables, and curves. Methods capable of detecting more than one compound, and simple effective ways of obtaining contaminant concentrations from calibration data were two of the many objectives sought for titrimetric methods prior to their inclusion into the modified Hach kit. None of these new methods used are original; they merely represent adaptations and/or modifications of common titrimetric procedures.

The Periodic Acid (Redox) Method for 1,2 Glycols is one example of a titrimetric method incorporated into the modified Hach kit. In this test, periodic acid is used for the selective oxidation of organic compounds with hydroxyl groups on adjacent carbon atoms (Kritchfield, 1963). Ethylene glycol and propylene glycol are two such examples. Periodate oxidation of α-hydroxylamines, compounds having hydroxyl and amino groups on adjacent carbon atoms, may also be determined this way. Ethanolamine, another chemical from Environment Canada's spills priority list, is such a compound. The reaction principle is illustrated below.



$$R-\overset{OH}{\overset{|}{C}}-\overset{OH}{\overset{|}{C}}-R' + IO_4^- \longrightarrow RCH{=}O + R'CH{=}O + IO_3^- + H_2O$$

In the Periodic Acid Method for ethylene glycol, two moles of formaldehyde are formed by adding a measured excess of periodic acid. The oxidation reaction is complete in 20 - 25 minutes at room temperature. The reaction mixture is rendered slightly alkaline with saturated sodium bicarbonate; an excess of potassium iodide is introduced; and the iodine liberated by the excess periodate is then consumed by a measured excess of sodium arsenite. The As(III) is then titrated with a standard iodine solution. Starch is used as the indicator.

To simplify calculations for contaminant content, repetitive testing was performed and appropriate calibration curves were constructed. The spill responder need only titrate to an endpoint, record the volume of titrant used, and cross reference that value to a calibration table for contaminant content in soil and water systems. Listed in Table 2 is a compilation of titrimetric methods which have been tested and evaluated, and have met specific test criteria for use in the Level II analytical system.

Conclusion

To further complement Environment Canada's Chemical Hazards Emergency Countermeasures Program for hazard level monitoring, person-portable analytical instrumentation systems capable of in-situ detection of hazardous materials are being developed. The Hach kit is presently being modified to include testing procedures for a variety of chemicals from Environment Canada's spills priority list. Emphasis is being placed on those methods capable of detecting hazardous materials in water, and soil. Repetitive testing and calibration of colorimetric methods for use with the Hach's spectrophotometer have resulted in meterscale overlays being developed. Similar testing of titrimetric methods has resulted in calibration curves and tables being developed for specific compounds. Future work will include ongoing testing and evaluation of methods, preparation of a test procedures manual, developing the appropriate chemical packaging, and inventories for the Hach kit.

TABLE 1

MODIFIED HACH KIT COLORIMETRIC METHODS

TEST	COMPOUNDS DETECTED FROM ENV. CAN. SPILLS LIST	REAGENTS NEEDED	COMMENTS	REFERENCE
2,4-Dinitrophenylhydrazine for Ketones and Aldehydes	Acetone Methyl ethyl ketone Methyl isobutyl ketone Formaldehyde n-Butyraldehyde iso-Butyraldehyde	2,4-Dinitrophenylhydrazine Potassium hydroxide Methanol Pyridine Hydrochloric acid	Absorbance read at 480 nm.	Kritchfield, F.E.
Tetracyanoethylene for Aromatics	Benzene Toluene Styrene Ethyl benzene Cumene o-Xylene p-Xylene m-Xylene p-Terphenyl	Tetracyanoethylene Methylene chloride Acetone Chloroform	Absorbance read at 440 nm.	Schenck, G.H. and Ozolins, M.
4-Aminoantipyridine for Phenols	Phenol Cresol Nonylphenol	Hach kit reagents	Absorbance read at 460 nm.	Hach Kit Manual.
ASTM D1942-80	Morpholine	37% Formaldehyde Sodium borate Carbon disulfide Copper sulfate Triton X-100	Absorbance read at 440 nm.	ASTM.
o-Tolidine	Hydrogen Peroxide	o-Tolidine Sodium acetate Ethanol Ferrous sulfate	Absorbance read at 450 nm.	Feigel, F.
p-Dimethylaminobenzaldehyde	Urea	Ethanol Hydrochloric acid p-Dimethylamino benzaldehyde	Absorbance read at 425 nm.	Watt, G.W. and Chrisp, J.D.
Fujiwara Test	Carbon tetrachloride Chloroform Ethylene dibromide	Ether Pyridine Sodium hydroxide	Absorbance read at 500 nm.	Burke, T.E. and Southern, S.
Malathion-Copper	Malathion	Carbon tetrachloride Alcohol Hydrochloric acid Copper sulfate Sodium hydroxide Sodium chloride	Absorbance read at 418 nm.	Sutherland. G.L.

* ENV. CAN: ENVIRONMENT CANADA

TABLE 2 MODIFIED HACH KIT TITRIMETRIC METHODS

TEST	COMPOUNDS DETECTED FROM ENV. CAN. SPILLS LIST	REAGENTS NEEDED	COMMENTS	REFERENCE
Periodic Acid for 1,2 Glycols	Ethylene glycol Propylene glycol Ethanolamine	Sodium bicarbonate Starch, Iodine Potassium Iodide Sodium hydroxide Periodic acid, sodium arsenite	Color change: purple to red	Kritchfield. F.E.
Thorin for Sulfates	Aluminum sulfate Ammonium sulfate Copper sulfate Potassium sulfate Sodium sulfate Zinc Sulfate	Barium chloride Thorin Amberlite IR-120 Hydrochloric acid Ammonium hydroxide Anhydrous alcohol	Color change: orange to pink	Analytical Methods Manual.
Mercuric Nitrate for Chlorides	Aluminum chloride Ammonium chloride Calcium chloride Ferric Chloride Potassium chloride Sodium chloride Sodium chlorate Zinc chloride	Mercuric nitrate Nitric acid S-diphenylcarbazone/ xylene cyanol FF	Color change: blue to purple	Standard Methods.
Mercuric Nitrate for Chlorides	Polychlorinated Biphenyls (PCBs)	Above plus: Naphthalene Sodium metal, Nitric acid, Sodium phosphate Bis(2 methoxy ethyl) ether	Color change: blue to purple	Ruttan, J.T.
Mercuric Acetate	Styrene Vinyl Acetate	Mercuric acetate Methanol, Chloroform Sodium bromide Potassium hydroxide Phenolphthalein	Color change: clear colorless to pink	Kritchfield, F.E.

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SOIL GAS INVESTIGATIONS FOR VOLATILE SUBSURFACE CONTAMINANTS: CASE STUDIES IN KANSAS, USA

Thomas A. Runyon and Glenn M. Thompson
Tracer Research Corporation

ABSTRACT

Tracer Research Corporation has developed a technique for delineating subsurface volatile organic chemical(VOC) contamination. The technique involves sampling and analyzing shallow(1-3m) soil gas for the presence of VOC's. Contaminated groundwater and/or soil acts as a source of VOC's and a chemical concentration gradient is established between the source and the ambient air resulting in the vertical diffusion of contaminants through the vadose zone.

This technique was used at two separate sites in Kansas to determine the areal extent and relative magnitude of volatile organic contamination in the subsurface. The soil gas data was also used to determine contamination sources and migration directions. At the first site, a trichloroethene(TCE) contamination plume was mapped extending over 1,600 feet from a previously suspected source. A second source of TCE was located in the process and the areal extent of contamination was determined by soil gas sampling. The second site contained a source of carbon tetrachloride (CCl_4) emanating from the vicinity of a grain elevator. A plume of CCl_4 over 3000 feet long was mapped in the soil gas.

INTRODUCTION

The method of detecting and delineating groundwater contamination by soil gas analysis has become increasingly popular in the last several years. By sampling soil gas in the vadose zone, plume characteristics such as areal extent, chemistry, place of origin, and migration direction can be assessed. This data can then be used to place monitoring wells in locations which will optimize plume observation.

Tracer Research Corporation has developed and applied soil gas analysis to more than 200 contaminated sites throughout the United States. Results from two sites in southeastern Kansas will be the topic of this paper.

The first site to be discussed is located in southeastern Kansas. This site contains several sources of Trichloroethene (TCE). TCE was first identified in supply wells on the eastern boundary of the industrial site. Objectives of the soil gas investigation were to locate the sources, determine contaminant migration directions, and define the areal extent of TCE contamination emanating from these sources.

The second site located in south-central Kansas contains a source of Tetrachloromethane(CCL4). The soil gas investigation objectives were to determine the direction of contaminant migration and, define the areal extent and relative magnitude of subsurface contamination.

BACKGROUND ON THE METHODOLOGY

The presence of volatile organic chemicals (VOCs) in shallow soil gas indicates the observed compounds may either be in the vadose zone or in groundwater below the probe. The soil gas technology is most effective in mapping low molecular weight halogenated solvent chemicals and petroleum hydrocarbons possessing high vapor pressures and low aqueous solubilities. These compounds readily partition out of the groundwater and into the soil gas as a result of their high gas/liquid partitioning coefficients. Once in the soil gas, VOCs diffuse vertically and horizontally through the soil to the ground surface where they dissipate into the atmosphere. The contamination acts as a source and the above ground atmosphere acts as a sink, and typically a concentration gradient develops between the two. The concentration gradient in soil gas between the source and ground surface may be locally distorted by hydrologic and geologic anomalies (e.g. clays, perched water); however, soil gas mapping generally remains effective because distribution of the contamination is usually broader in areal extent than the local geologic barriers and is defined using a large data base.

The presence of geologic obstructions on a small scale tends to create anomalies in the soil gas-groundwater correlation, but generally does not obscure the broader areal picture of the contaminant distribution.

SAMPLING AND ANALYTICAL EQUIPMENT

TRC utilized a field van equipped with a specialized hydraulic mechanism capable of driving and withdrawing soil gas probes. Power for the operation of all field equipment was provided by two built-in 110 volt(AC) generators. The field van also contained two Varian 3300 gas chromatographs capable of analyzing soil gas and water samples on packed as well as capillary columns. TRC has developed a gas chromatograph modification (patent pending) that allows direct injection of soil gas and water samples without using preconcentration or purge and trap techniques. The gas chromatographs utilized the following detectors:

a) electron capture: for analysis of halogenated hydrocarbons such as 1,1,1 trichloroethane, trichloroethene, tetrachloroethene.

b) flame ionization: for analysis of hydrocarbons such as methane,benzene, toluene, xylenes. and total hydrocarbon content.

Soil gas probes consisted of seven foot lengths of galvanized steel pipe fitted with detachable drive points. An electric vacuum pump was used to withdraw soil gas.

SAMPLING PROCEDURE

Soil gas sampling probes were driven up to nine feet into the subsurface. The probes were then withdrawn several inches in order to free the drive point from the probe and permit the flow of soil gas. The vacuum pump, equipped with a calibrated flow monitoring gauge, was then attached to the above ground end of the probe by means of a metal reducer, silicone, and polyethylene tubing. Soil gas samples were collected in 10ml glass syringes by inserting the syringe needle through the silicon portion of the tubing and withdrawing 1 to 10ml of soil gas directly from the gas stream. Soil gas was subsampled (duplicate injections) in volumes ranging from 1 to 1500 ul, depending on the VOC concentration at any particular location. The samples were analyzed immediately by direct injection into the gas chromatograph. Results were typically available within five minutes.

RESULTS AND DISCUSSION

Southeastern Kansas Site

Trichloroethene (TCE) contamination was found in the groundwater beneath an industrial park in southeastern Kansas. TCE was first detected in the park's water supply wells near the eastern boundary of the site.

Tracer Research Corporation performed a soil gas survey as part of an ongoing investigation of the contamination problem.

Objectives of the investigation were a) locate the source(s) of groundwater contamination within the industrial park; b) define the areal extent of contamination; c) determine the direction(s) of contaminant migration.

The soil gas survey involved the sampling of 75 soil gas probes. The probes were placed throughout the site on a grid spacing of approximately 500 feet. Soil gas was collected at depths ranging from 1.5 to 5 feet.

The data from 44 sampling locations is plotted on figure 1. Isoconcentration contours were generated for the purpose of establishing contamination parameters such as migration direction(s) and areal extent.

Figure 1 shows two separate areas of TCE soil gas contamination occuring in the north and south portion of the site.

In the north contaminated area, the highest vapor concentration observed was (19ug/l TCE). The soil gas contours suggest that contamination is migrating east. This corresponds to the approximate direction of groundwater flow in this area. TCE contamination has spread approximately 1600 feet east from the area of maximum soil gas contamination. The TCE soil gas plume does not extend beyond the supply wells where this compound was first detected in the groundwater. This may indicate that pumping of the water supply wells has effectively intercepted and stopped eastward migration of the plume. TCE was not detected 400 feet west of the area of maximum soil gas contamination. This was expected as this is the direction opposite of groundwater flow.

The second source of TCE is located approximately 2000 feet south of the previously defined area of contamination. TCE contamination as determined by soil gas sampling in this area is limited to approximately an 800x400 foot area. The soil gas data does not indicate significant contaminant migration.

South-Central Kansas Site

Carbon tetrachloride (CCl_4) has been extensively used in the past as a fumigant in grain elevators. Many of the grain elevators have now been indentified as sources of CCl_4 leading to soil and groundwater contamination.

Tracer Research Corporation performed a soil gas survey in south-central Kansas to investigate several grain elevators which were suspected sources of CCl_4. The results indicate a single plume of CCl_4 which probably originated from the grain elevator property.

The soil gas investigation involved sampling in the vicinity of the grain elevator to a) determine if CCl_4 contamination is a problem b) define the extent of contamination if discovered and c) determine contaminant migration direction(s).

Soil gas samples were collected on a grid spacing of approximately 500 feet. The samples were collected at depths ranging from 2 to 5 feet. The data from 42 sampling locations appears on Figure 2.

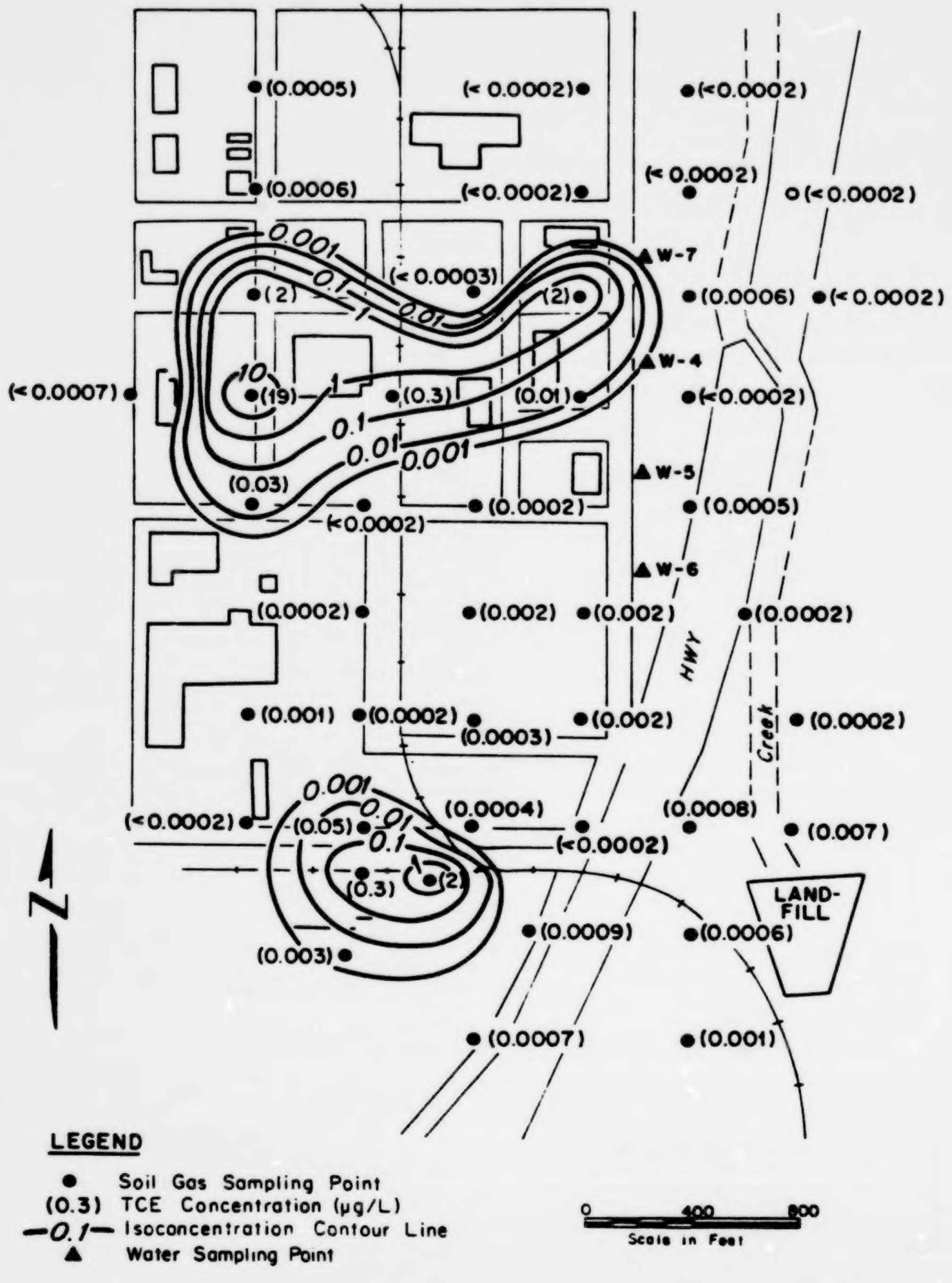
TRC detected maximum CCl_4 contamination (90 ug/l)in the soil gas 50 feet south of the grain elevator. CCl_4 concentrations vary by five orders of magnitude from this location to the southern extent of contamination (0.006 ug/L).

CCl_4 is migrating approximately due south. Contamination extends approximately 3400 feet south, 600 feet east, and 1600 feet west of location with the highest soil gas reading.

FIGURE 1.

SOUTHEASTERN KANSAS SITE

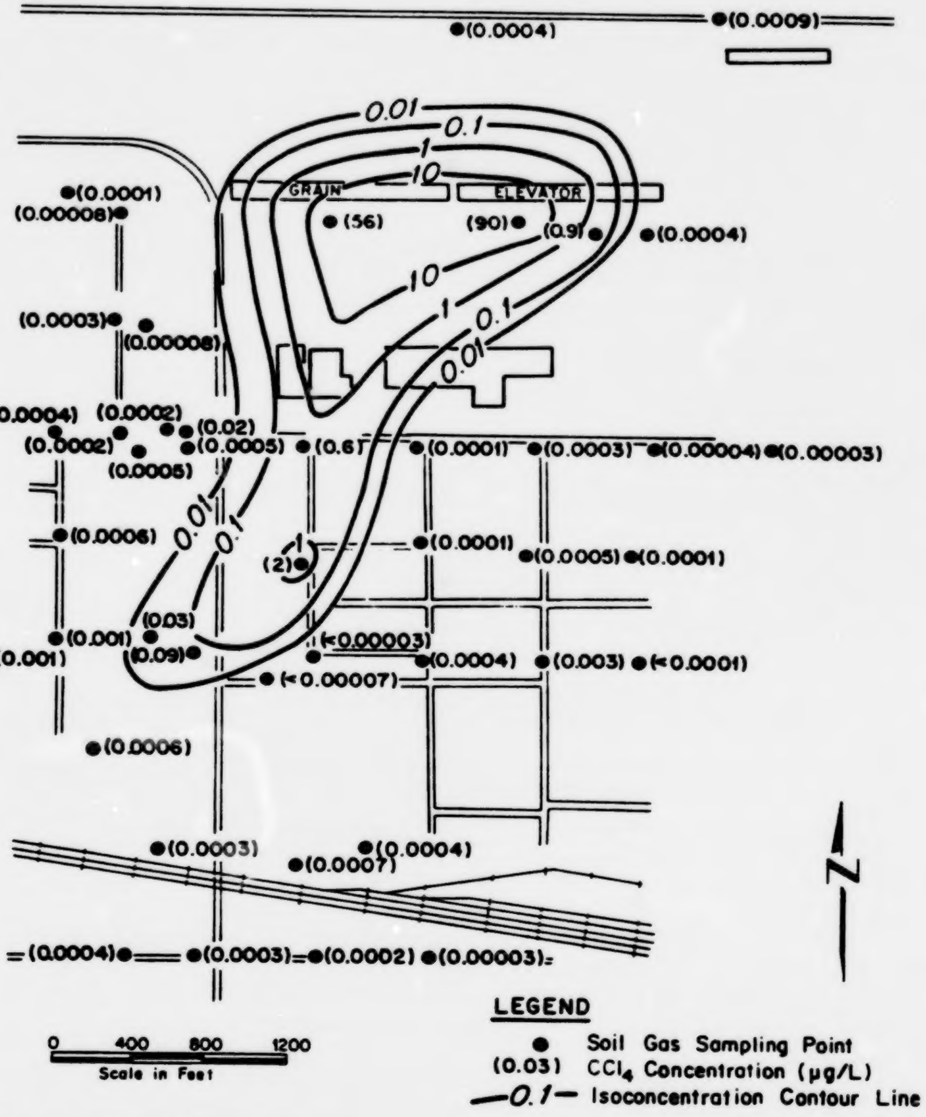
Trichloroethene (TCE) Isoconcentration Contour Map


(0.0005)
(< 0.0002)
(<0.0002)
(0.0006)
(<0.0002)
(< 0.0002)
(<0.0002)
0.001
0.1
1
0.01
(< 0.0003)
(2)
(2)
W-7
(0.0006)
(< 0.0002)
W-4
(< 0.0007)
10
(19)
1
(0.3)
(0.01)
(<0.0002)
0.1
0.01
0.001
W-5
(0.03)
(0.0002)
(0.0005)
(<0.0002)
W-6
(0.0002)
(0.002)
(0.002)
(0.0002)
HWY
(0.001)
(0.0002)
(0.0003)
(0.002)
Creek
(0.0002)
0.001
0.01
(<0.0002)
(0.05)
(0.0004)
(0.0008)
(0.007)
0.1
(<0.0002)
1
(0.3)
(2)
LAND-FILL
(0.0009)
(0.0006)
(0.003)
(0.0007)
(0.001)
N
LEGEND
Soil Gas Sampling Point
(0.3) TCE Concentration (µg/L)
0.1 Isoconcentration Contour Line
Water Sampling Point
0
400
800
Scale in Feet

Tracer Research Corporation

FIGURE 2.

SOUTH CENTRAL KANSAS SITE
Carbon Tetrachloride (CCl_4) Isoconcentration Contour Map


(0.0004)
(0.0009)
0.01
0.1
1
10
GRAIN
ELEVATOR
(0.0001)
(0.00008)
(56)
(90)
(0.9)
(0.0004)
10
1
0.1
0.01
(0.0003)
(0.00008)
(0.0004)
(0.0002)
(0.02)
(0.0002)
(0.0005)
(0.0005)
(0.6)
(0.0001)
(0.0003)
(0.00004)
(0.00003)
0.01
0.1
(0.0006)
1
(2)
(0.0001)
(0.0005)
(0.0001)
(0.03)
(0.001)
(0.001)
(0.09)
(<0.00003)
(0.0004)
(0.003)
(<0.0001)
(<0.00007)
(0.0006)
(0.0003)
(0.0004)
(0.0007)
(0.0004)
(0.0003)
(0.0002)
(0.00003)
N
0
400
800
1200
Scale in Feet
LEGEND
● Soil Gas Sampling Point
(0.03) CCl4 Concentration (µg/L)
—0.1— Isoconcentration Contour Line

TRACER RESEARCH CORPORATION

A lack of sampling locations in the upgradient direction precludes an accurate assesment of the northern plume boundary. Two soil gas samples collected north of the grain elevator indicated a rapid decline in CCl_4 contamination in this direction.

CONCLUSION

At the southeastern Kansas site, TCE contamination from a previously suspected source was traced 1600 downgradient from the area of highest concentration. A second TCE source was identified and contamination was detected within an 800x400 foot area.

In south-central Kansas, CCl_4 contamination emanating from a grain elevator was detected and quantified in the soil gas. The contamination extended 3400 feet south of the grain elevator.

Soil gas analysis provides an initial assessment of subsurface contamination. The data can be used in the placement of monitoring wells to insure optimum plume observation.

BIOGRAPHICAL SKETCHES

Thomas A. Runyon received his Bachelor of Science in geology from Northern Arizona University in 1985. Since that time he has been employed as a field geologist and soil and lab field technician. He is currently employed as a hydrogeolist for Tracer Rsearch Corporation. He is experienced in all aspects of soil gas technology including sample collection and analysis, directing soil gas investigations, and interpreting data obtained from such investigations. He is also currently working on his M.S. degree in hydrology.

Glenn M. Thompson is the founder and president of Tracer Research Corporation, a hydrochemical consulting firm specializing in tracer technology and subsurface contaminant investigations. He earned his B.S.(1970) and M.S.(1973) in geology from the University of Rhode Island and Memphis State University, respectively. He received his Ph.D. in geology from Indiana State University (1976). He served on the faculty of the Department of Hydrology at the University of Arizona from 1977 to 1983. While at the university, he was principal investigator on 10 major research grants that resulted in publications on tracer technology, subsurface gas diffusion, solute transport in groundwater, and tracer monitoring of hazardous waste burial sites.

A Portable Instrument for Multiple Compound Detection and Analysis

W.J. Buttner[1], R.D. Battin[1], S.E. Becker[1], D.S. Domin[1], C.R. Gentry[1], W.P. McDowell[2], W.R. Penrose[1], Lt.JG. S. O'Malley[4], V.C. Stamoudis[1], J.R. Stetter[3], Lt. J.O. Stull[4], R.J. Voogd[2], and S. Zaromb[1]

(1) Environmental Research Division, Argonne National Laboratory, Argonne, IL
(2) Electronics Division, Argonne National Laboratory, Argonne, IL
(3) Transducer Research, Inc., Naperville, IL
(4) U.S. Coast Guard, Office of Research and Development, Washington, D.C.

Background

In response to a need by the United States Coast Guard and other agencies to monitor levels of toxic chemical vapors frequently encountered in chemical spills, we have been developing a portable toxic vapor analyzer. Details of an earlier prototype instrument have been previously described (1). This instrument measures 16 independent signals (i.e. chemical parameters) and identifies and quantitates a sample by a comparison of its response to a predetermined library (so called "chemical parameter spectroscopy", or CPS) (2). The present instrument model, which weighs ca. 9.0 Kg (including battery pack) and has dimensions of 31.5 X 32.1 X 23.5 cm, is truly portable. It has been designed to be used with only a few operator-initiated commands and has microprocessor controlled data acquisition, analysis, and identification. Moreover, emphasis was placed upon designing a rugged instrument able to easily withstand the levels of abuse likely to be encountered in the field. Prototypes have been delivered to the United States Coast Guard for evaluation.

Instrumentation and Methods

Instrument Design and Construction

There have been extensive improvements in the instrument since the first prototype was introduced. During the early stages of development, it had been necessary to test various electronic circuit designs and instrument configurations. Thus, circuitry which had been constructed in-house was utilized. While the use of homemade electronics is essential in order to evaluate performance and to demonstrate the viability of an instrument of this nature, such circuitry is not as rugged as would be necessary for use in the field nor would it be conducive for large-scale production. Moreover, the instrument was constructed as a single unit, which rendered it difficult to service, and most problems associated with the instrument's performance were directly related to the actual physical construction.

In the past two years, the problems associated with the initial portable units have been addressed. The connectors were chosen for ruggedness. All electronics are mounted on computer-designed printed-circuit boards and equipped with test points to facilitate servicing by qualified technicians. All of the elctronic subsystems of the unit are laid out on individual circuit boards. This modular design allows for rapid replacement of boards in the event of a failure of one of the subsystems and renders the instrument easy to service. The entire unit is packaged inside a sturdy 31.5 X 32.1 X 23.5 cm steel carrying case. A removable and rechargeable battery pack fits in the bottom panel of the carrying case. The total unit weighs 9 Kg.

Microprocessor Control of the Portable Unit

In the original unit, microprocessor control was achieved utilizing the technology that was available in 1976. Data acquisition and analysis is now controlled by a high-speed, low-power, state-of-the-art microprocessor (CMOS 8088) with 64 Kbytes of memory. This microprocessor is essentially identical to that used in the IBM-PC. The unit may now be programmed in high level languages; it is now programmed in the computer code "C". The library searches are now performed at a rate of ca. 150 comparisons per minute versus a rate of ca. 15 comparisons per minute in the original unit. The operating software is directly accessible to an IBM-PC via a RS232 port. The unit, however, is not currently programmed to run via external computer control, but it can be. At present, 32 Kbytes of memory are used for the 25 compound library and algorithms. The unit is designed so that the memory can be expanded to 512 Kbytes without any modification of the hardware, thus allowing implementation of more sophisticated software. Data analysis is performed via comparison of the normalized response patterns of test runs to those stored in the library. The microprocessor computes the Euclidean distance between the 16 element vectors of the sample and library files. Identification and reliability are based upon closeness of fit; quantification is performed from a comparison of the net (not normalized) signals in the strongest channel between sample and the identified compound. The analysis algorithm is essentially identical to that described previously (1).

Probe Design and Features

Stored inside the top panel of the case is a hand-held sampler probe. The probe, which is a new feature in the instrument, allows for direct sampling of vapors on site. The probe is easily connected to the pneumatics and electronics of the instruments. Mounted directly inside the probe is an oxygen detector and combustible gas detector In the event that low levels of oxygen or high concentrations of combustible gases are encountered, both audible and visual alarms will be set off. A red and green LED indicates unsafe levels of combustible gas or oxygen, respectively. The alarm thresholds may be adjusted to appropriate levels by trained personnel.

Sensors and Sensor Arrays

As with the earlier prototype instrument, the detection technology employs three-electrode amperometric sensors. The sample gas is monitored simultaneously by an array of four sensors, each biased to a different operating potential. The array comprises two sensors with gold working electrodes biased to -200 mV and +300 mV (vs. a Pt-air reference), one sensor with a platinum working electrode biased to +200 mV, and a commercial electrode (National Draeger, model 45950k) with a platinum black working electrode biased to 0 mV. The modular design also encompasses the sensor array which is replaced as a unit. The array housing is 12.7 X 10.6 X 7.6 cm and includes the filament chamber as well as the potentiostat and current amplifier circuit board. Besides monitoring the currents induced by untreated samples, the responses of the four sensors to the sample pyrolyzed by heated noble metal filaments were measured. Operationally, sequential sensor responses are determined with the sample gas passing over a Rh filament heated to 750°C and to 1000°C and over a Pt filament heated to 900°C. Such treatments convert electrochemically inactive compounds like benzene into electrochemically active products. The observed sensor response to the pyrolyzed sample was found to be highly reproducible and dependent only upon the composition of the sample gas. Thus, by measuring the response of the four sensors for each of the four modes of operation, 16 signals (the "chemical parameters") are obtained. The typical concentration range for gas detection is between ca. 10 to 200 ppm, although lower detection limits are attainable. The current response for each sensor induced by NO_2 is depicted in figure 1A. Normalization of the net current yields the depicted histogram. Such histograms are graphic representations of the data stored in the instrument's library to which test runs are compared. As indicated in figure 2, a compound will generate an unique response pattern.

Operating Modes and Performance Evaluation

Figure 3 depicts the assembled instrument in its present configuration. As a self-contained unit, it is simple to operate and does not require extensive training. Operator commands, which are displayed on a liquid crystal display (with a backlight to facilitate use in the dark), are initiated by four push button switches located on the front panel. The commands are simple and self-explanatory. The instrument is able to perform in three operator-controlled modes. These three modes are: 1) IDENT (identify), 2) UNIV (universal) and 3) SELECT. In the IDENT mode, the sample gas is qualitatively analyzed to identify the toxic vapor present and to determine its concentration. SELECT mode is designed to verify the presence or absence of a specific (operator selected) chemical in the environment. UNIV mode monitors the sample for the presence of any undetermined compounds. It had been determined that for libraries of up to 25 compounds, the instrument correctly identifies test samples with a 90% efficiency (1). Using an advanced algorithm, an

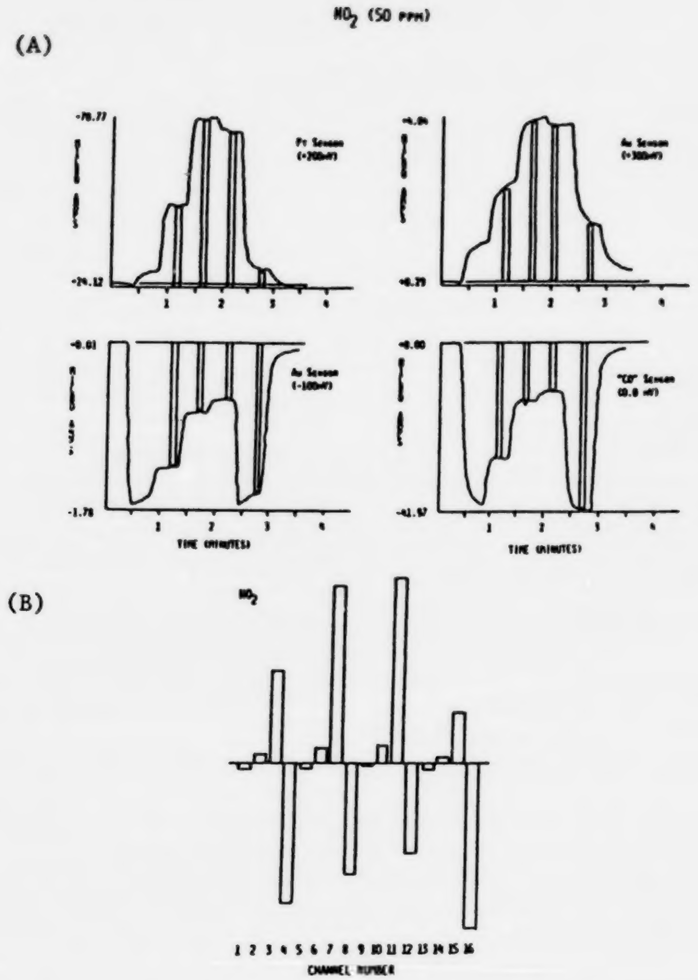


FIGURE 1 (A) Current time response induced by 50 ppm of NO_2. The array was exposed to 20 seconds of air followed by the sample. For 30 seconds the sample was not pyrolyzed, followed in order with 30 seconds of pyrolysis over a Pt filament (900°C), 30 seconds of pyrolysis over a Rh filament (750°C), 30 seconds of pyrolysis over a Rh filament (1000°C), and 30 seconds with the filaments off. (B) The resulting histogram was obtained from the normalized currents. Channels 1, 5, 9, and 13 were obtained from the low potential Au sensor, channels 2, 6, 10, and 14 were obtained from the high potential Au sensor, channels 3, 7, 11, and 15 were from the Pt sensor, and channels 4, 8, 12, and 16 were obtained from the commercial sensor. Channels 1-4 are with the Pt filament on, channels 5-8 are with the Rh filament on (750°C), channels 9-12 are with the Rh filament on (1000°C), and channels 13-16 are in the absence of filament pretreatment.

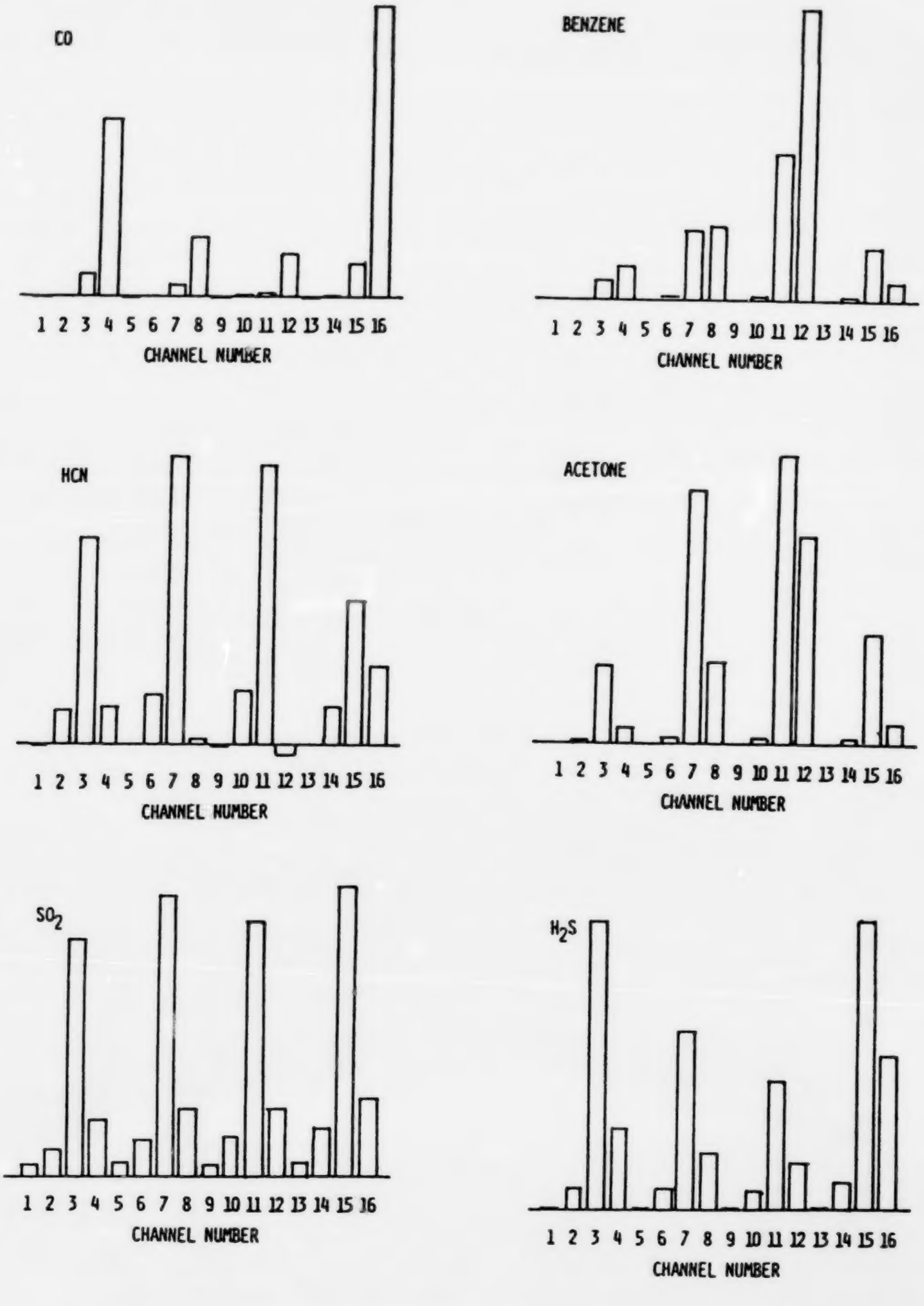


FIGURE 2 CPS histograms of selected compounds.

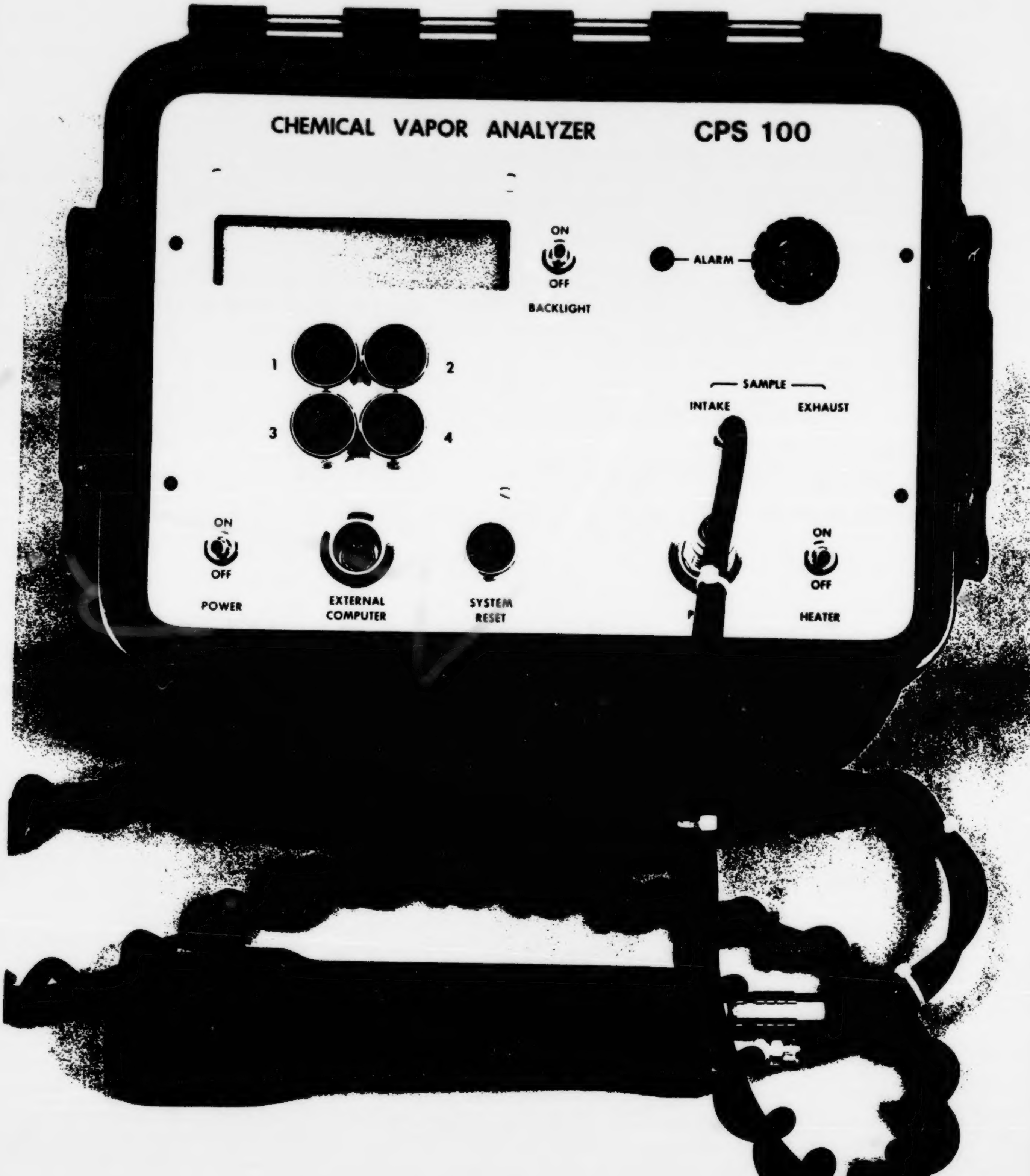

CHEMICAL VAPOR ANALYZER
CPS 100
ON
OFF
BACKLIGHT
ALARM
1
2
3
4
SAMPLE
INTAKE
EXHAUST
ON
OFF
POWER
EXTERNAL COMPUTER
SYSTEM RESET
ON
OFF
HEATER

FIGURE 3 Photograph of the portable toxic vapor analyzer.

identification efficiency of 80% was obtained for 65-compound libraries and a 90% efficiency was obtained for a library with a selective group of 59 compounds (3).

Conclusion

An accurate, lightweight, truly portable toxic vapor analyzer has been designed and constructed for industrial applications. It is a rugged instrument capable of performing an accurate analysis within 5 minutes. Customized libraries can be readily installed in the instrument to fulfill the specific needs of a client. While this particular unit was designed to monitor levels of toxic chemicals commonly encountered at spill sites or near storage vessels, the technology which was developed can be applied to other applications. Applications include monitoring the environment around chemical plant sites, or detecting solvents associated with clandestine drug laboratories.

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THE CONTINUING DEVELOPMENT OF A VEHICLE PORTABLE ANALYTICAL SYSTEM

W.J. Mills
S.L. Ross Environmental Research Ltd.
Ottawa, Ontario

A.M. Bobra
Environment Canada
Ottawa, Ontario

Introduction

Following a major chemical spill it is imperative to have analytical systems which are capable of rapid, on-site determinations of what has been spilled and of its concentration in air, water or soil. Recognizing that these analytical requirements were not adequately met in most spill situations, the Environmental Emergencies Technology Division (EETD) of Environment Canada began a program in 1980 to develop analytical methods suitable for spill response. Since then, the vehicle portable analytical system (Level 3 system) has been considered to be the system most capable of providing rapid, on-site qualitative and quantitative information. The Level 3 system involves equipment normally found in a fixed laboratory and operated by a trained operator (1). The instrumentation is mounted in a van along with support equipment to make it completely self sufficient. The system makes use of the available microprocessor technology and user friendly software to allow it to be operated under emergency conditions and obtain results useful for spill response.

The Level 3 system can identify chemicals in the following spill situations:

1) one pure highly toxic chemical is spilled. (e.g. benzene)
2) a mixture of pure chemicals is spilled. (e.g. acetone,toluene and benzene)
3) a chemical which is a mixture of compounds is spilled. (e.g. PCB's)
4) a pure chemical and a chemical mixture is spilled. (e.g. PCB's in Methanol)
5) a complex spill of several chemical mixtures. (e.g. PCB's and naptha)
6) when any of the above are spilled on a complex media such as soil.

The chemicals to be analysed for by the system were chosen from Environment Canada's top 150 priority chemicals. Preliminary work on the Level 3 analytical system has been described by Bobra (2).

Developmental work on the Level 3 System

This paper describes recent work performed on the vehicle portable analytical system by S.L. Ross Environmental Research Ltd. for EETD. The Level 3 system chosen by EETD for development consists of a Perkin-Elmer Sigma 2000 Gas Chromatograph (GC) and an associated data system mounted in a 1986 Ford cargo van. The van is equipped with an air conditioner, power generator, line regulator, propane heater and an air filtration/pressurization system. Initially only the data system was line regulated. The line regulator was required in order to prevent fluctuations in the power line voltage from affecting the computer. The air filtration and pressurization unit consists of an air intake on the upper right side of the van, a Buffalo 2VEH air blower and a filter frame in which up to 12 filters may be installed (e.g. prefilter, activated carbon, soda lime, molecular sieves and HEPA etc.). This pressurization system allows the interior atmosphere of the van to be isolated from a chemically contaminated atmosphere, providing an extra measure of protection for the operators. The van's atmospheric integrity can be manintained at wind speeds of up to 32 km/hr. The technical details of the above equipment are summarized in Table 1. Pictures of the van showing the exterior and interior are shown in Figures 1 and 2.

Instrumentation

Three detectors have been supplied with the GC, a flame ionization detector (FID), photoionization detector (PID), and an electron capture detector (ECD). The FID detects most organic compounds while the PID provides increased sensitivity for aromatic molecules and some inorganic compounds. The ECD is selective for halogenated compounds such as polychlorinated biphenyls (PCB's). The GC conditions used for analysis with packed and open tubular columns are shown in Table 2.

The analytical procedures employed at a chemical spill site should be rapid, reproducible and involve as little sample manipulation as possible. Ideally one should be able to collect the environmental sample of interest and inject aliquot into the GC without pre-analysis cleanup. The Sigma 2000 GC can use three different sample introduction methods which enables it to analyse water, soil and air samples.

Water samples can be analysed on the Sigma 2000 GC by both standard flash evaporation (direct injection) or headspace analysis.

For analysis by direct injection a J&W Scientific DB-5 (polymethyl(5% phenyl)siloxane) "Megabore" open tubular column

Table 1: Technical specifications for equipment installed in the Level 3 van.

NUMBER	COMPONENT	MANUFACTURER	P/N	DESCRIPTION
1	Generator System			
(a)	Generator	Onan (McGraw Edison)	6.5 NH-3CR	6.5 kW, 2 cylinder, 4 cycle, gasoline
(b)	Spark Arrester Muffler	Onan (McGraw Edison)	-	-
(c)	Generator Enclosure	Davis Engineering Limited	-	2 layers 5/8" plywood, lined with 2" Soundfoam "M" with Tedlar
2	Benches			
(a)	Left	Stanley Vidmar	MT-120	Laminated maple 1 3/4 x 24 x 120
(b)	Right	Stanley Vidmar	MT-120	Laminated maple 1 3/4 x 30 x 120
(c)	Legs	Davis Engineering Limited	-	
3	Shelves			
(a)	Wall	Hovey Industries	-	General Purpose
(b)	Under Bench	Hovey Industries	-	General Purpose
4	Cabinets/Drawers			
(a)	Four Drawer Cabinet	Stanley Vidmar	MODEL 175	Includes Latches
(b)	Overhead Storage	Hovey Industries	8175182-1	Includes Mounting Brackets
(c)	Two Drawer Cabinet	Lista	B309.4	Includes Latches/Locks
(d)	"Doghouse"	Davis Engineering Limited	-	Built into Vehicle
5	Air Conditioner	Duo-Therm	610015	Royal Penguin, 13,500 Btu/hr
6	Heating System			
(a)	Furnace	Duo-Therm	65941-001	40,000 Btu/hr in, 32,000 Btu/hr out
(b)	Duct Work	Davis Engineering Limited	-	4" Flexible Fibreglass Duct, Plywood cover
(c)	Propane Tank	Manchester	-	35 lb "Underslung"
(d)	Vents	-	-	4" Diameter, Adjustable Flow Direction

Table 1: (continued)

NUMBER	COMPONENT	MANUFACTURER	P/N	DESCRIPTION
7	Gas Bottle Brackets			
(a)	Large	Davis Engineering Limited	-	-
(b)	Small	Davis Engineering Limited	-	-
8	Electrical System	Commander		
(a)	Circuit Breaker	Commander	B870	5 Breakers(2x15A, 2x20A, 1x30A)
(b)	Main Disconnect	-	F202IN	-
(c)	Generator/Vehicle Plug	-	L1430P & L1430C	Female on Generator Side
(d)	Power Conditioner	Sola	63-13-220	2000 VA Rating
9	Installation Equipment			
(a)	Shock Mounts (GC)	Barry Controls	UC-2040-6	-
(b)	Shock Mounts (DD)	Barry Controls	UC-1010-T-4	-
(c)	Shock Mounts (SPC)	Ontario Rubber	M100A	-
10	Rubber Matting	Ontario Rubber	Close Rib	-
11	Stools	Williams/Wilson	Model 2050	Adjustable Seat Height/Back
12	Filtration System			
(a)	Rear Plenum	Davis Engineering Limited	-	Teflon Runners -
(b)	Support Frame	Davis Engineering Limited	-	Four drawers for various filter materials/configuration
(c)	Filter Drawer	Ridalco/Davis Engineering Ltd.	-	-
(d)	Exhaust Plenum	Davis Engineering Limited	-	-
(e)	Blower	Buffalo Forge Co.	2 VEH	Variable Speed
(f)	3" Hose	Zagerman's	"Flexaust"	-
(g)	4" Hose	Lindian Motor Sales	-	-

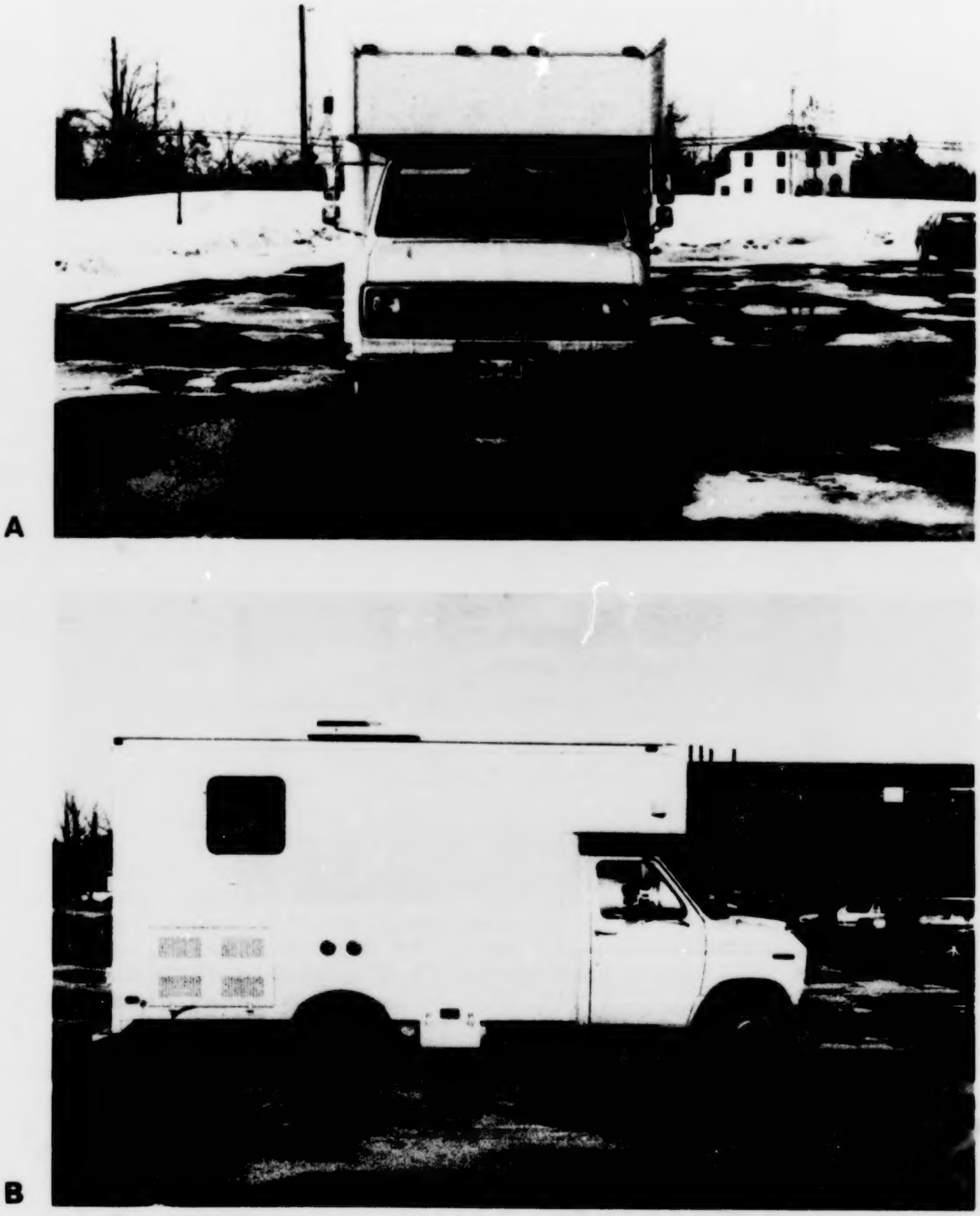


Figure 1: Exterior of the Van used for the Level 3 analytical system. a) Front view b) side view.

Figure 2: Interior of the Van used for the Level 3 analytical sytem.

Table 2: Gas Chromatography Conditions used by the Sigma 2000 GC

Temperature Program

Initial T = 48 C ----> raise T @ 15 C/min. ----> hold at 220 C
hold for 8 minutes to 220 C for 20 minutes

(T = Temperature)

Total GC analysis time = 39.5 minutes

Injectors

Flash evaportion at 270 C
Headspace: equilibration at 80 C, injector at 270 C

Detectors

FID = 270 C PID = 250 C ECD = 375 C

Column Conditions

Open Tubular GC

Direct Injection analysis of water or solvent samples
Column: J & W Scientific DB-5 "Megabore"
(0.53 mm i.d. X 30 m long)
Carrier Gas: Nitrogen @ 11 ml/ minute
Valco ZDV splitter, 2 detectors
Makeup Gas Flowrates: FID = 15 ml/ minute
PID = 25 ml/ minute
ECD = 75 ml/ minute

Packed Column GC

Headspace analysis of water samples or thermal desorption of adsorbed chemicals
Column: Supelco 60/80 Carbopack B/ 1% SP-1000
(2 mm i.d. X 6 ft long)
Carrier Gas: Nitrogen @ 40 ml/ minute
No makeup gases required

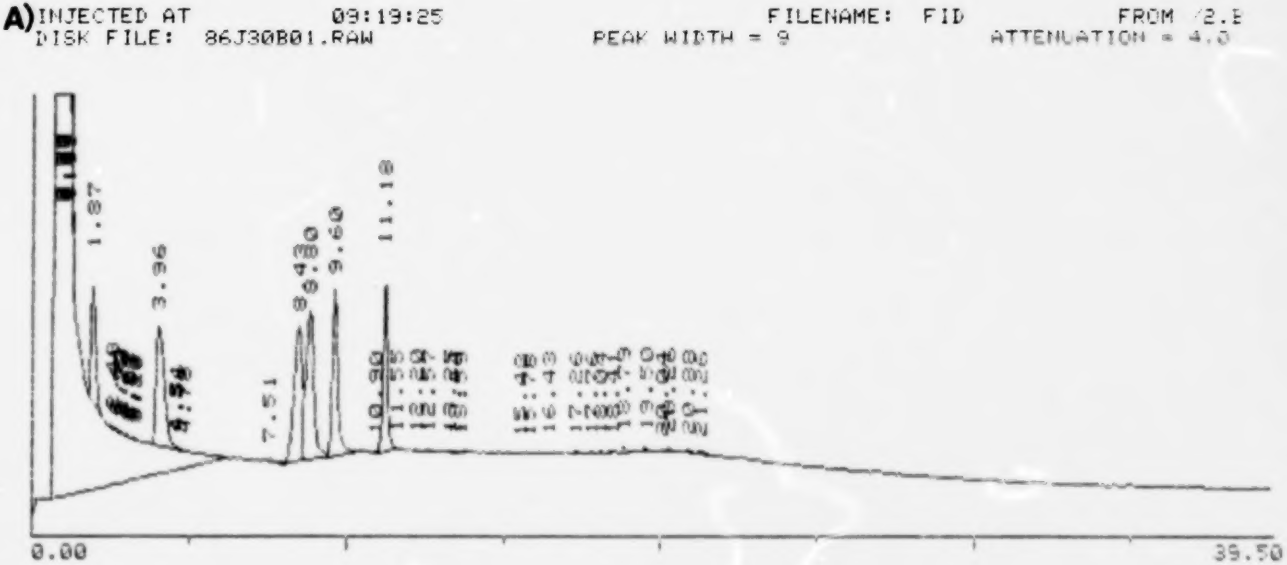
with nitrogen as the carrier gas is used. The stationary phase of this column is inert, two uL of water may be injected directly onto the column without damage occurring to the column. This procedure allows water samples to be analysed without preliminary sample cleanup. This reduces the analysis time and increases accuracy. The effluent from the Megabore column is split to two detectors by a Valco 1/16" ZDV tee. The split ratio of the tee is adjustable by changing the length or inside diameter (i.d.) of the tubing to the detectors. In routine operation simultaneous FID/PID detection is used. If a water sample is expected to contain halogenated compounds FID/ECD detection can be used. When the concentration of organic compounds in a water sample is very low or compounds which may interfere with the analysis are present, sample cleanup and concentration can be affected by solvent extraction. The chromatograms obtained from the direct injection analysis of an aromatic mixture on the DB-5 column with simultaneous FID/ECD detection are shown in Figures 3 and 4.

For the Level 3 system quantitation is performed using the external standardization method. In this method the injection volume must be reproducible and the linearity of the detector response must be verified for each chemical of interest. The injection volume using a Hamilton 10 uL syringe was found to have a precision of ± 5%. The calibration curve obtained for morpholine (Figure 5) illustrates the linear response of the FID.

Volatile organics elute very quickly from the DB-5 column. As a consequence, some compounds may not be resolved or properly quantitated. Water samples which contain volatile organic compounds may be accurately analysed using the headspace analysis technique. The Sigma 2000 GC is equipped with an HS-6 headspace sampling accessory. For analysis using this accessory a 2 mL aliquot of the water sample is pipetted with an Oxford Macropipette into a headspace vial and the vial + septum are crimp sealed. The vials are then equilibrated for a minimum of 20 minutes at 80 degrees C in the HS-6 sampler. The vial is pressurized with nitrogen for 0.5 minutes and the headspace gas in the vial is then sampled. Analysis takes place on a Supelco 60/80 Carbopack B/1% SP-1000 packed column with nitrogen as the carrier gas. The column effluent is monitored by one of the three detectors. Figure 6 shows the chromatogram obtained for the headspace analysis of a water sample containing a variety of volatile organic compounds. The precision of the injection volume for the HS-6 sampler was found to be ± 1.2% . The calibration curve obtained for benzene in water (Figure 7) illustrates the linear response of the FID.

Soil samples can be analysed in the Sigma 2000 GC by headspace analysis or by the direct injection of the solvent from

A)

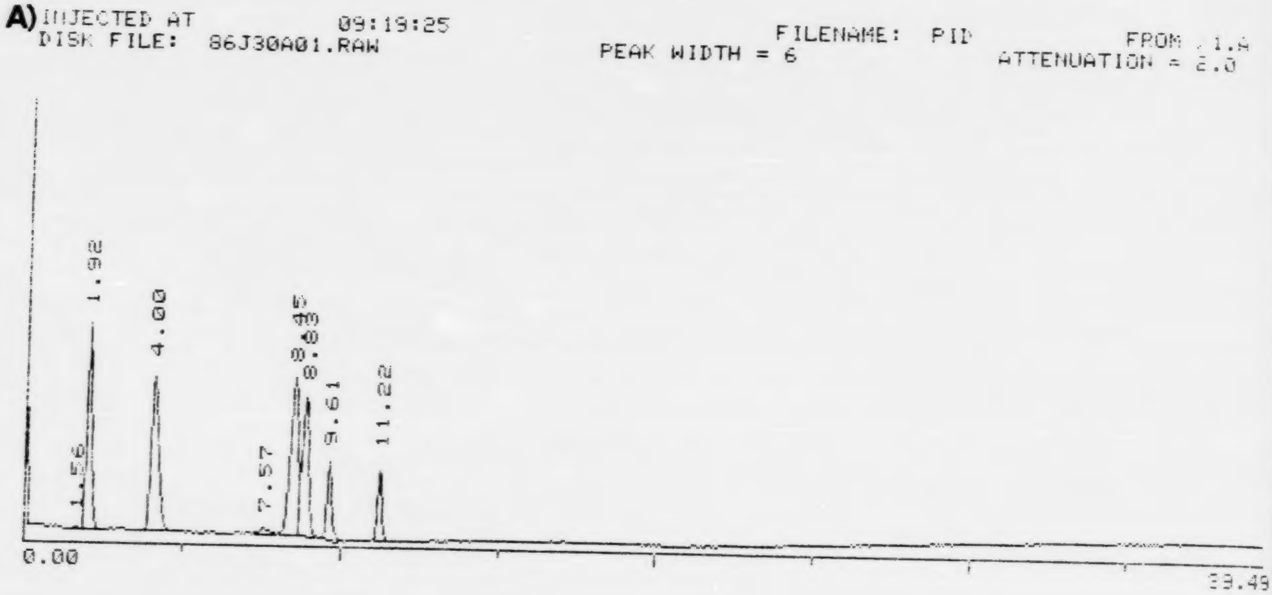


```
INJECTED AT          09:19:25                FILENAME:  FID          FROM /2.B
DISK FILE:  86J30B01.RAW           PEAK WIDTH = 9               ATTENUATION = 4.0
```

```
B)DISK FILE: 86J30B01.RAW    FROM / 2.B/   INJECTED AT:          09:19:25

                                                CH=       PS=   1
FILE   1     METHOD  0     RUN    4     INDEX   4

PEAK#              AREA%         RT        AREA BC

  1               71.171       0.81    1036670 08
  2                0.795       0.87      11571 06
  3                4.988       0.97      72663 06
  4                1.784       1.05      25979 06
  5                5.597       1.09      81526 07
  6                1.403       1.87      20436 05―――――― BENZENE
  7                0.001       2.48         13 05
  8                0.004       2.7          62 06
  9                0.005       2.78         74 06
 10                0.002       2.97         21 06
 11                0.002       3.03         37 06
 12                0.004       3.13         54 06
 13                0.009       3.2         131 07
 14                2.805       3.96      40860 06 ――――― TOLUENE
 15                0.006       4.51         90 06
 16                0.024       4.56        347 06
 17                0.055       7.51        799 02
 18                3.105       8.43      45231 02 ――――――  ETHYL BENZENE
 19                3.274       8.8       47679 02 ― ―――  p-XYLENE
 20                2.568       9.6       37411 03 ――――――  STYRENE
 21                0.008      10.9         120 02
 22                2.045      11.18      29789 08 ――――――  PROPYL BENZNE
```

Figure 3: GC chromatogram (a) and report file (b) for direct injection analysis of an aromatic mixture (FID detection).

A)



```
INJECTED AT              09:19:25
DISK FILE:  86J30A01.RAW                          FILENAME:  PID              FROM   1.A
                                          PEAK WIDTH = 6                 ATTENUATION = 2.0
```

B)

```
DISK FILE: 86J30A01.RAW     FROM / 1.A/   INJECTED AT:              09:19:25

                                                         CH=        PS=   1
FILE   1       METHOD  0      RUN     1      INDEX   1

PEAK#             AREA%          RT            AREA  BC

  1                0.205        1.56             204 02
  2               19.096        1.92           18981 03 ———— BENZENE
  3               23.906        4.             23763 01 ———— TOLUENE
  4                0.807        7.57             802 01
  5               24.301        8.45           24155 02 ———— ETHYL BENZENE
  6               18.694        8.83           18582 03 ————  p-XYLENE
  7                6.978        9.61            6936 01 ————  STYRENE
  8                6.013       11.22            5977 01 ————  PRQPYL BENZNE

TOTALS           100.                          99400
```

Figure 4: GC chromatogram (a) and report file(b) for the direct injection analysis of an aromatic mixture (PID detection).

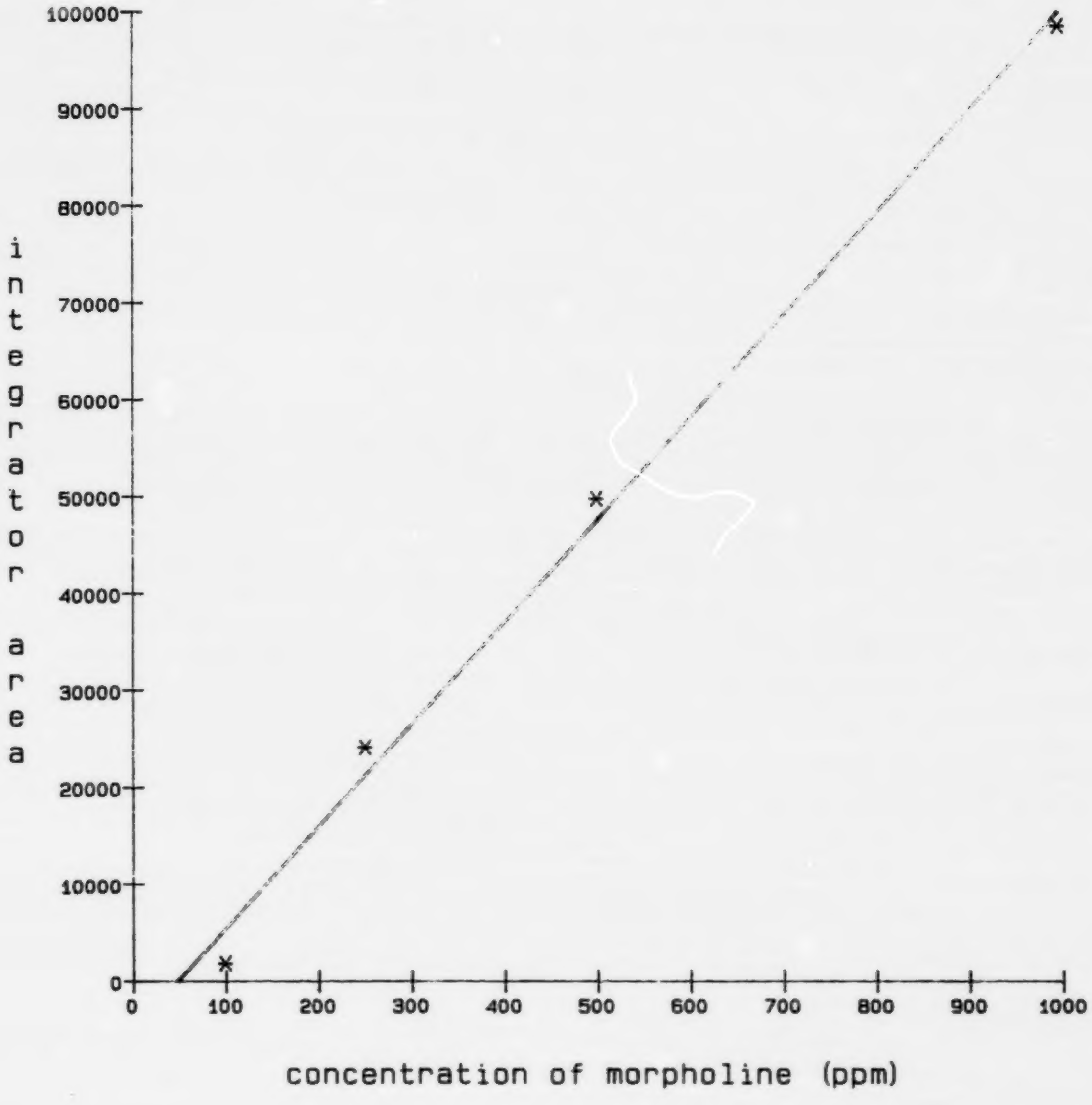
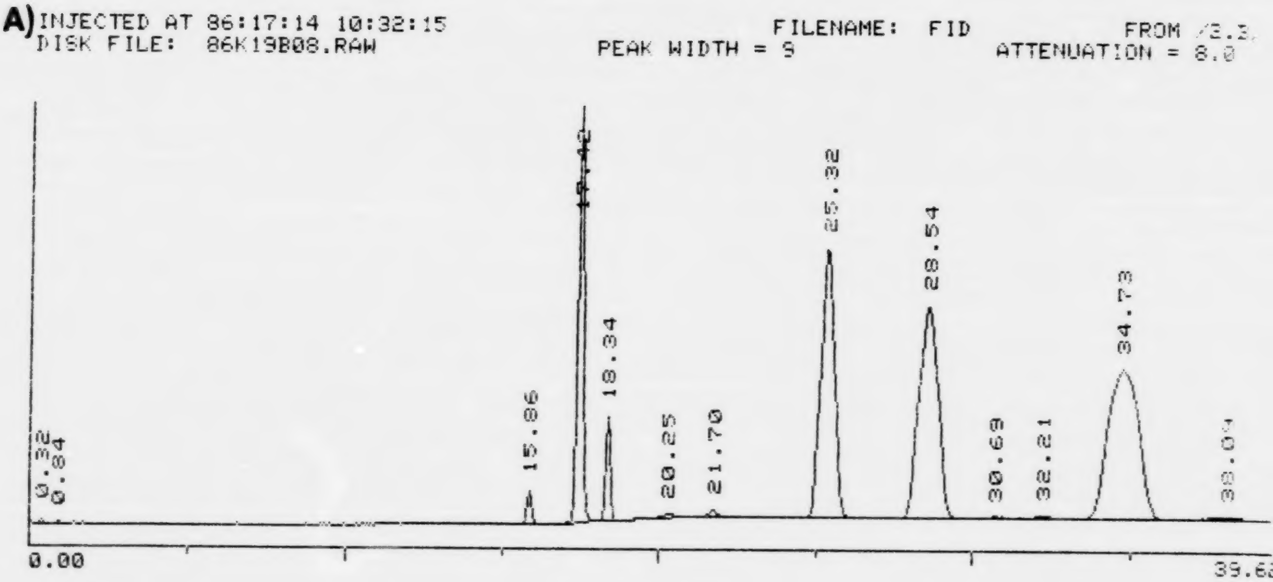


Figure 5: FID calibration curve for direct injection analysis of Morpholine.



```
B)DISK FILE: 86K19B08.RAW    FROM / 2.B/   INJECTED AT: 86:17:14 10:32:15

                                                   CH=       PS=   1
FILE    1      METHOD  0      RUN    3     INDEX   3

PEAK#              AREA%          RT        AREA BC

   1               0.071        0.32         899 01
   2               0.016        0.84         193 01
   3               0.961       15.86       12110 01———————  HEXANE
   4              15.161       17.42      190892 01——————  BENZENE
   5               3.094       18.34       38966 01 —————  HEXANE
   6               0.359       20.25        4517 01————   TETRACHLOROETHYLENE
   7               0.248       21.7         3124 01 ——————TOLUENE
   8              23.423       25.32      294943 01——————— ETHYL BENZENE
   9              26.395       28.54      332361 01 ——————
  10               0.128       30.69        1608 02
  11               0.313       32.21        3940 03
  12              29.473       34.73      371122 01———————PROPYL BENZENE
  13               0.358       38.09        4502 01

TOTALS            100.                   1259177
```

Figure 6: GC chromatogram (a) and report file (b) for the headspace analysis of an organic mixture in water (FID monitoring).

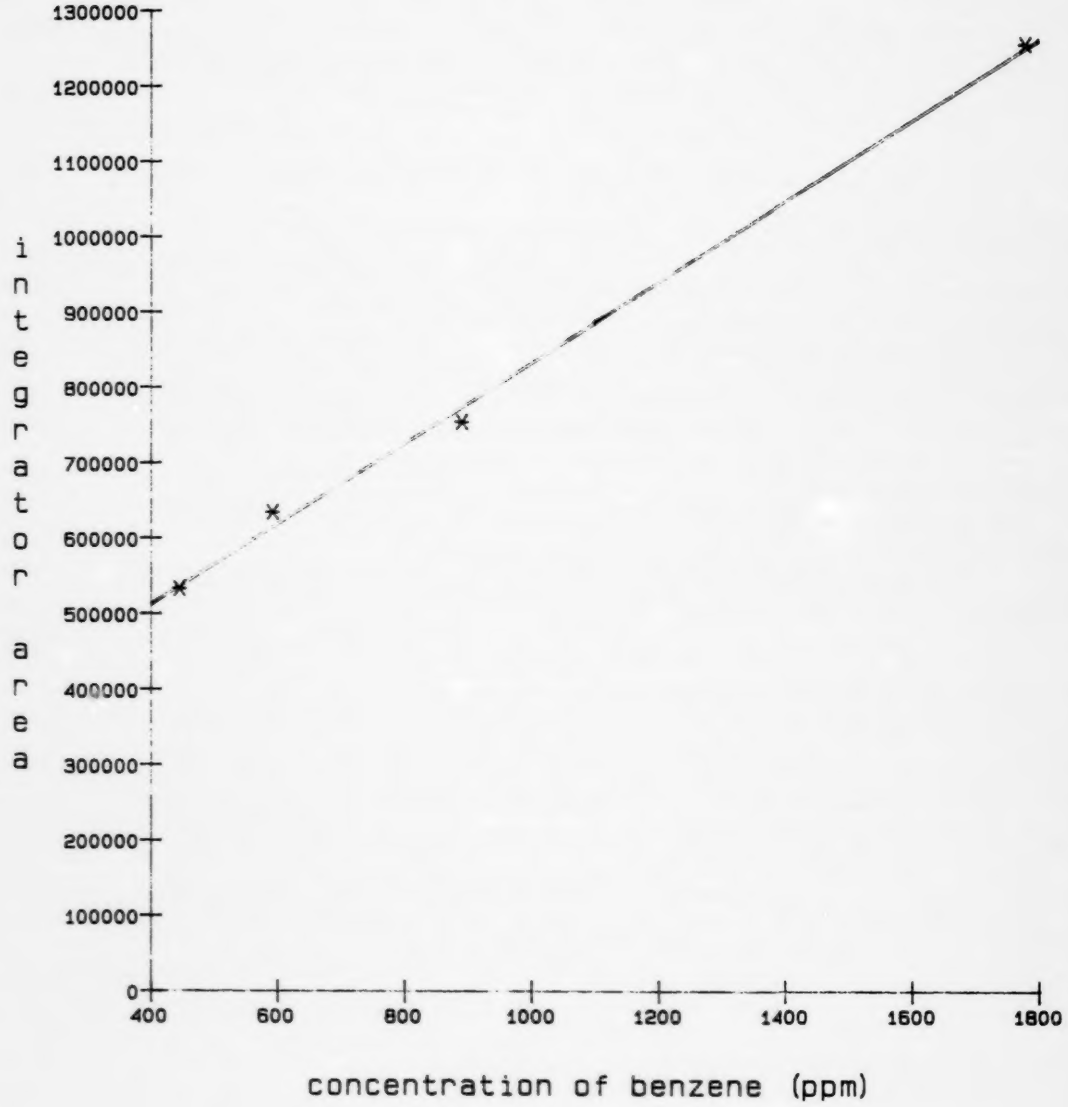


Figure 7: FID calibration curve for headspace analysis of benzene in water.

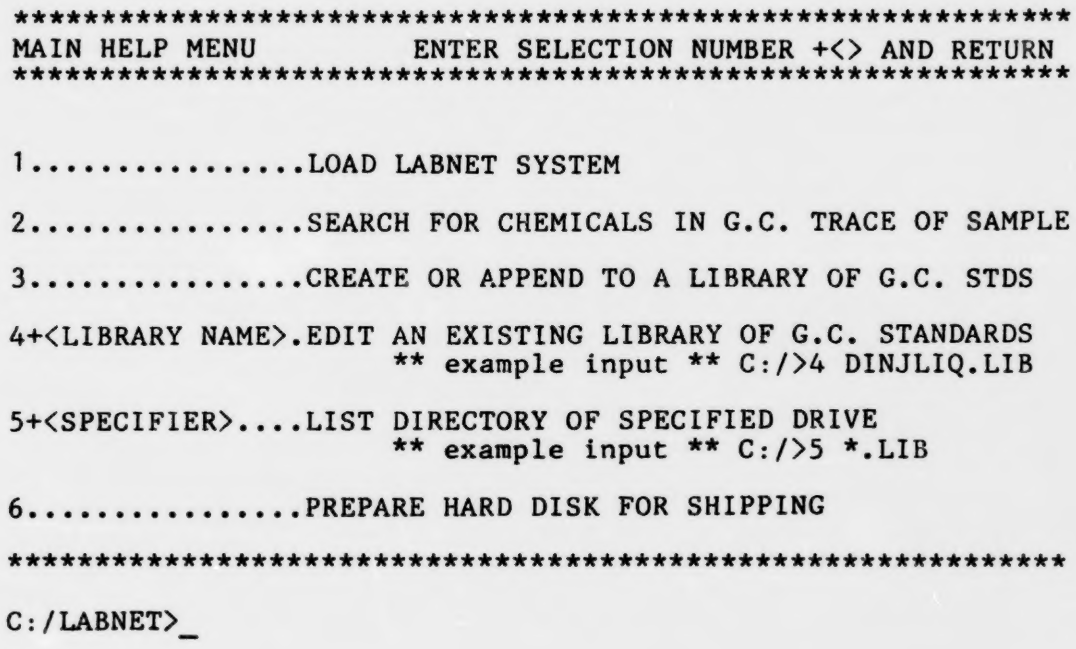
a solvent extraction of the soil. For headspace analysis a known quantity of soil is equilibrated in the headspace vial and the headspace gas is analysed. Alternatively, a known amount of soil can be extracted with an organic solvent (such as hexane). An aliquot of the organic extract is then analysed by direct injection on the Megabore column. Factors which may affect the quantitation of chemicals in soils are moisture content and the variability of adsorption onto different soils. Sandy soils will retain far less organics than peats, which are rich in humic acids.

Airborne contaminants can be analysed drawing a known amount of air through an adsorbent filled tube. Heating of the tube will free the adsorbed chemicals which are then analysed. In the Level 3 system a Gilian air sampling pump is used to collect the air samples onto Tenax GC adsorbent. The Tenax filled tubes are desorbed in an Analabs PTD-132A thermal desorber. The desorbed chemicals are sampled via the heated gas sampling valve on the Sigma 2000 GC and analysed on the Supelco SP-1000 column.

Data System

The data system for the Level 3 analytical system is composed of Spectra-Physics 4270 dual channel integrator interfaced with an IBM PC/XT microcomputer. The PC/XT computer is equipped with a Hercules graphics card, Spectra-Physics Labnet chromatography software system and a 10 megabyte hard disk for data storage. Hard copies of the GC data are printed out on an Epson dot matrix printer. The GC and data system have been vibration/shock mounted to prevent damage occurring during transit. User friendly menu driven software has been developed for the vehicle portable analytical system by R. Belore of S.L. Ross Environmental Research Ltd. This software permits a relatively inexperienced operater to use the data system. The data system software controls data acquisition, data storage and the building of the chemical data library used for the identification and quantitation of unknowns. The main "HELP" menu from which these processes are accessed is displayed in Figure 8

The data acquisition parameters which include chart speed attenuation, stop acquisition time and file name are entered by the operator from within the Labnet software. A remote relay from the Sigma 2000 GC to the integrator starts data acquisition a soon as an injection is made on the GC. At the end of a GC run data files are created and stored on the hard disk. There are tw types of data files; the raw data file (filename.raw) contain the chromatogram itself (e.g. Figures 3a & 4a) and the repor file (filename.rpt) contains the retention times and integrate areas of the major peaks in the chromatogram (e.g. Figures 3b &



```
***************************************************************
MAIN HELP MENU         ENTER SELECTION NUMBER +<> AND RETURN
***************************************************************

1................LOAD LABNET SYSTEM

2................SEARCH FOR CHEMICALS IN G.C. TRACE OF SAMPLE

3................CREATE OR APPEND TO A LIBRARY OF G.C. STDS

4+<LIBRARY NAME>.EDIT AN EXISTING LIBRARY OF G.C. STANDARDS
                 ** example input ** C:/>4 DINJLIQ.LIB

5+<SPECIFIER>....LIST DIRECTORY OF SPECIFIED DRIVE
                 ** example input ** C:/>5 *.LIB

6................PREPARE HARD DISK FOR SHIPPING

***************************************************************

C:/LABNET>_
```

Figure 8: Main "HELP" menu for the Level 3 data system.

4b). The data files stored on disk can be displayed at any time by using the "DISPLAY" key.

The identification and quantitation of unknown chemicals at a spill site is made by comparing the chromatogram(s) obtained on site with the data in chemical library for the appropriate injection method. This data library contains the following information for each chemical; the retention time (R.T.) of the chemical, the retention time for a standard under the same conditions and the relative response factors (R.R.F.) of the chemical for the 3 detectors. The GC is calibrated by running a standard sample of known composition. The standard solution used for direct injection analysis is 200 ppm toluene,150 ppb tetrachloroethylene in methanol. To allow this standard solution to be used in the field it is stored in sealed glass ampoules until needed. The standard for headspace analysis is an aqueous solution of 100 ppm acetone,100 ppm butanol and 20 ppm tetrachloroethylene. This standard is prepared prior to use and stored in sealed headspace vials. The calibration runs allow the computer to correct for any changes in retention times or split ratio, etc. After an unknown sample has been analysed with the GC a computer search of the appropriate chemical library is performed to identify and quantitate the chemical(s) in the sample. The chemicals in a sample are identified on the basis of their retention times compared to the standard. Quantitation is made on the basis of the relative response factor for each chemical.The software used for the computer search prompts the operator for the following information:

1) the calibration run's report file.
2) the detector trace to be searched (e.g. FID, PID, ECD).
3) the injection method (e.g. direct injection, headspace etc.).
4) the unknown sample's filename.

Figure 9 shows the prompts issued in the search routine. The results from the computer search of a test chromatogram are shown in Figure 10. A manual describing the operation of the GC and the data system has been prepared for EETD by S.L. Ross Environmental Research Ltd. (3).

Conclusion

To date the Level 3 system has performed extremely well under varying climatic conditions. It has been successfully operated at temperatures ranging from +5 degrees C to +35 degrees C and high humidity with no major problems. Originally the the GC was not connected to a regulated power supply, however it was found to be susceptible to "spikes" in the line voltage especially during thunderstorms. Another line regulator has been installed to rectify this problem. The low flow rates to the

```
SPECIFY DETECTOR RESPONSE TO BE COMPARED BY SELECTING
APPROPRIATE CODE NUMBER
       1 - FOR PID
       2 - FOR FID
       3 - FOR ECD
                 ENTER CODE No. - 1


SPECIFY SAMPLE INTRODUCTION METHOD USED BY SELECTING
APPROPRIATE CODE NUMBER
       1 - FOR DIRECT INJECTION OF A LIQUID
       2 - FOR DIRECT INJECTION OF A GAS
       3 - FOR HEADSPACE ANALYZER
                 ENTER CODE No. - 1


ENTER FILE NAME CONTAINING RESPONSE OF UNKNOWN CHEMICAL -
    test.dat
```

Figure 9: Prompts issued by data system software for computer library search.

First Sample Search Pass

```
UNKNOWN SAMPLE FILE NAME - test.dat
NUMBER OF MAJOR PEAKS IN UNKNOWN SAMPLE - 2
TOTAL NUMBER OF PEAKS IN UNKNOWN SAMPLE - 4
DETECTOR RESPONSE BEING SEARCHED - PID

CHEMICALS WHICH MAY BE IN SAMPLE  APPROX.CONC. RET TIME DIFF
                                    [mg/l]        [min]
    METHANOL                       .000E+00       .000
    STYRENE                        .586E+00       .030
```

Repeat of Search using New Parameters

```
TO REPEAT THE SEARCH USING EITHER

    A NEW RETENTION TIME MATCHING WINDOW
or  A NEW PEAK AREA CUTOFF VALUE

   ENTER - 9 - OTHERWISE JUST RETURN : 9

PRESENT RETENTION TIME MATCHING WINDOW IS +-  .02 %
PRESENT PEAK AREA CUTOFF IS - 1000.

ENTER NEW R.T. MATCHING WINDOW : .04

ENTER NEW PEAK AREA CUTOFF : 500

CHEMICALS WHICH MAY BE IN SAMPLE  APPROX.CONC.  RET TIME DIFF
                                    [mg/l]         [min]
    METHANOL                       .000E+00        .000
    HEXANE                         .174E+02        .040
    STYRENE                        .586E+00        .030
    o-XYLENE                       .291E+02        .060
```

Figure10: Results from the computer search of a test chromatogram.

Table 3: Chemicals which the Level 3 analytical system can currently detect in water by direct injection analysis

Acetic acid
Acetic anhydride
Acetone(propanone)
Adipic acid(hexanedioic acid)
Benzene
Benzoic acid
Butanal
Butanols: 1-butanol
  isobutanol
  tert-butanol
Caprolactam
Carbofuran pesticide
Carbon tetrachloride
Chlordane
Chlorobenzene
Chloroform(trichloromethane)
Cresols: ortho-
  meta-
  para-
Cyclohexane
Dicamba pesticide
Dichlorobenzene: ortho-
  meta-
  para-
Dimethyl terephthalate
Dinoseb
Ethanol
Ethylbenzene
Ethylene dibromide
Ethylene dichloride
Ethylene glycol
2-Ethylhexanol
n-Hexane
Isopropanol(1-methylethanol)
Isopropylbenzene
Malathion
Maleic anhydride
Methanol
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
Methylene chloride(dichloromethane)
MCPA
Morpholine
Naptha
Nonyl phenol
PCB's- 1242-
  1254-
  1260-
Pentachlorophenol
Phenol
Phthalic anhydride
Styrene
Tetrachloroethylene
Terphenyls ortho-
  meta-
  para-
Toluene
1,1,1-Trichloroethane
Trifluralin
Vinyl acetate
Xylenes ortho-
  meta-
  para-

Table 4: Chemicals which the Level 3 analytical system can currently identify in water by headspace analysis.

Acetic acid
Acetone
Acrylonitrile
Benzene
Butanals: 1-butanal
    isobutanal
Butanols: 1-butanol
    isobutanol
    tert-butanol
Carbon disulfide
Carbon tetrachloride
Chloroform
Cyclohexane
Dichlorobenzene: ortho-
    meta-
Ethanol
2-Ethylhexanol
Ethyl benzene
Ethylene dibromide
Ethylene dichloride
Isopropanol
Isopropylbenzene
n-Hexane
Methanol
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
Methylene chloride
Naptha
Propylene oxide
Styrene
Toluene
1,1,1-Trichloroethane
Turpentine
Vinyl acetate

detectors from the Megabore column necessitated the installation of an FID makeup gas. This resulted in improved resolution and increased sensitivity. The experience of other mobile van operators prompted us to obtain a second power generator to be kept as a backup (4).

At present the chemical libraries for the direct injection and headspace analysis of water samples are nearing completion. The library for chemicals which can be analysed by direct injection is shown in Table 3. The headspace analysis library is listed in Table 4. Work is now in progress on further developing the analytical methodology for soil and air samples. Field testing of the Level 3 system is to begin in the near future. The results obtained to date have indicated that the Level 3 system should be able to provide qualitative and quantitative information of the chemical(s) involved wthin hours of arriving at a spill site. This will allow the spill responders to choose the most effective response measures.

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"MONDAY MORNING QUARTERBACKS", TURPIN, RODNEY D.; CAMPAGNA, PHILIP R., U.S. ENVIRONMENTAL PROTECTION AGENCY, ENVIRONMENTAL RESPONSE TEAM, EDISON, NEW JERSEY, 08837, USA

INTRODUCTION

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide technical assistance to On-Scene Coordinators (OSC), Regional Response Teams (RRT), EPA Headquarters, and Regional Offices, as well as other United States and Foreign Governmental Agencies in the area of emergency environmental issues such as chemical spills and uncontrolled hazardous waste sites.

This paper briefly describes some of the more interesting learning experiences shared by the authors on various response activities. Although this paper is technical in nature, the subject is approached from the lighter side. The theme of each experience will be either Occupational Health and Safety or Air Monitoring; and it will include such activities as train derailments, hazardous waste sites, and a Malathion Fire in Sri Lanka.

EXPERIENCES

1. "Hazardous Waste Site Activities Reduce Site Airborne Concentrations"

A. DRUM SITE: New England

Site Description: This site was located in a rural area of New England surrounded by both hardwood and evergreen trees. It consisted of approximately 5,000 - 7,000 drums containing various organic waste. Although several of the drums were either rusted through or used as a .22 caliber pistol/rifle target by local resident(s), airborne organic concentration were low due to ambient air temperatures.

ERT Support Function: In addition to ERT's on-site air monitoring function, we were involved in various other phases of the operation: compatibility testing; on-site mobile laboratory analysis; site safety protocols; and projectile opening of small lab pack bottles.

Air Monitoring Activity: The air monitoring operation was a very visible function since it monitored both site conditions as well as private residential areas.

Since the site was located next to a major highway, it was decided to collect background samples up wind of the road when conditions were appropriate. The sampling activities took place in the late fall/early winter with background stations set up in a nearby public park surrounded by evergreen trees.

The real-time air monitoring instruments did not indicate elevated background concentrations within the park area and background samples were collected. However, on-site analysis of thermal desorption collection tubes did reveal that ambient background samples contained more organic contaminants than the site samples.

Obviously, background stations were relocated and did reflect a lower background level. However, the remaining questions were; Did the contaminants come from the evergreen trees or did the movement of air across the site remove the contaminants? The authors suggest that the trees were at fault and have not placed a background station in a park since this response.

B. TELEPHONE TREATING FACILITY: Eastern Coastal Area

Site Description: This site was located within an industrial park on a small tidal river in a Mid-Atlantic State. Even though the area was heavily industrialized, the citizens were concerned with their environment. Ten to Fifteen years ago a nearby river had been contaminated by a pesticide manufacturing facility which had an adverse impact on the fishing industry. Most of the river traffic was restricted to tug boats and barges. Drawbridges were the most popular way to transport automobile traffic across the river.

ERT Support Function: EPA Regional offices requested assistance in monitoring the site for potential on-site and off-site airborne contamination.

Air Monitoring Activities: Since some of the specific site contaminants produced at this location could be potentially found in the surrounding atmospheric conditions, background data appeared to be more important for this site than for most others. Unfortunately, the most ideal ambient temperature conditions (summer) also meant the highest relative humidity and increased automobile activity.

After several months of planning and waiting for the right atmospheric conditions, the trip took place. However, Mother Nature was not totally cooperative. While ambient air temperatures and wind velocity were appropriate, wind direction was not optimum during the limited sampling period.

As luck would have it, the wind direction caused the background station to be set up near the drawbridge. While past experiences have revealed that automobile traffic will have an adverse impact on the background concentrations, wind direction would not permit any other options.

A survey of the area with hand held real-time instruments indicated an area below the drawbridge (10 - 12 ft. under the roadway) would be a suitable location for a background sample. Thus, the long awaited sampling commenced and within a 4 hour sampling period something unscheduled happened. A tugboat passed by and the drawbridge raised - - not once but twice. In addition to this taking a long time (15 - 20 mins), it occurred during two peak traffic periods 8:00 a.m.-9:00 a.m. and 11:00 a.m.-12 noon. This caused cars and trucks to back up for approximately 1/2 - 1 mile on top of the background sampling station.

As you may have guessed, the on-site analytical Gas Chromatograph (GC) revealed that background levels were higher than site conditions. Once again, our air monitoring has shown that hazardous waste site activities reduce pollutants from the ambient air. At this point, we hope you agree that site monitoring is far more easier than many background surveys.

2. "YE OLDE ERT LAW: Murphy was an Optimist"

A. Recycling Facility - Northwest Area

Site Description: This 13 acre site was located in the Northwest portion of the West Coast in a residential/light industry area. The site was a recycling facility with various types of materials ranging from fly ash and scrap metal to organic waste contaminated with PCB's. The site consisted of approximately 70 storage tanks, 5000 drums, incinerator, laboratory, and waste lagoons just to name a few. What separates this site from other recycling facilities is that the acidity of some of the lagoons was below pH1.

ERT Support Function: ERT's support consisted of the following on-site activities: occupational health and safety protocols; air monitoring; compatability testing; removal/disposal techniques; on-site mobile laboratory protocols/support; and off-site analytical protocols/support.

Occupational Health and Safety Protocols: The specific site safety plan followed the guidelines given in the U.S. EPA, OERR, Standard Operating Safety Guides, November 84, and was modified to meet the specific needs of this site. The various site activities were conducted in Level "B" and "C".

Since all of the waste materials were required to be shipped out of the particular State for disposal, solidifying the organic liquid waste present in the lagoons was a necessity. Recognizing the location of the Northwest site, sawdust was selected as the natural cellulose material to accomplish this task. The actual mixing of the sawdust caused more of an occupational health and safety problem than did the engineering aspects.

A front end loader was selected as the mixing device and the operator used modified Level B protective equipment. The clothing consisted of the chemical resistant type, while the respirator was a supplied air type with the air tank affixed to the cab.

After several days of monitoring the breathing zone of the front end loader, the clean-up contractor's industrial hygienist reduced the respirator protection from air-supplied to air-purifier respirator.

In this case, the operator was hospitalized for several hours when the front end loader punctured a drum which released a toxic plume. This plume engulfed the operator and penetrated the air purifier. The concentrations were such that the individual was overcome and collapsed.

While the contractor's practice of selecting respirator protection is applicable for other industrial settings, it is not applicable for hazardous waste site operations. The U.S. EPA, OERR Standard Operating Safety Guide, November 1984, calls for the selection of respirators to be based on several factors, one of which is potential exposure.

B. SANITARY LANDFILL SAMPLING: Northeast, USA

Site Description: This site was located on the East Coast and was bordered on the south by the Atlantic Ocean and on the East by a canal. The site was surrounded by single and multiple family dwellings.

The site was an active sanitary landfill which included a small municiple waste incinerator. A short period before the monitoring was performed there were news stories in the local papers also concerning the illegal disposal of hazardous waste into sanitary landfills in the metropolitan area. Residents of the area had also complained of odors from the landfill.

ERT Support Function: ERT's task was to perform air sampling/monitoring at the landfill and community. Air samples were collected at the landfill, from gas vents, from possible leachate seeps, and in the community. The plan consisted of collecting air samples on various type of media (i.e., carbon, tenax, silica gel, etc.), air bags, and real-time monitoring with a Mobile Mass Spectrometer (MS/MS) unit.

The air samples were collected over a 6-8 hour period using personal sampling pumps at various flow rates with carbon, tenax, and silica gel collection tubes. In addition, air bag samples were collected from various sampling locations. The air bag samples were analyzed for methane gas using an organic vapor analyzer-flame ionization detector (OVA-FID) and vinyl chloride using a photoionization detector - gas chromograph (PID - GC). Standards for the vinyl chloride were prepared by diluting a certified vinyl chloride air standard cylinder using zero air and air bags.

It was during this analysis of vinyl chloride that Murphy's Law first appeared during this activation. Instead of shipping the Vinyl Chloride cylinders, it was decided to place the standard in 5 liter air bags and to make the field dilution from it. During the first day of analysis, the analyst observed that the peak area of diluted standards decreased over time. It was determined that the vinyl chloride was either bleeding from the bags or was decomposing. Therefore, an emergency call was placed back to the office and the air cylinder was immediately shipped to the site.

High Tide or Low Tide

Murphy's Law struck again. Note that some of the sampling team was born and raised around the Great Lake Area where the effect of the tides on water level is minimized. On the third day, the sample plan called for sampling these areas where vapors might be emitted from leachate. This was done by stationing pumps equipped with various media over possible leachate seeps. It was during the second inspection of pump locations that the effect of tidal activity was observed by the sampling team...the stations were gone. The pumps were found the next day during low tide...not working.

C. ABANDONED INCINERATION OPERATION: Great Lakes Area

Site Description: This site was located in a suburban area and consisted of contaminated soil and sludge. In addition, the site consisted of lagoons and a two acre area of buried drums. The sludge and soil contained C-46, C-56, C-58, C-48 and other chlorinated organics. The cleanup activities were being performed by a responsible party contractor.

ERT Support Function: The ERT was requested by the Region to develop and implement a community air monitoring plan and emergency action plan in case of a release. The ERT was also asked to review the cleanup contractor's air monitoring plan, and the health/safety practices of on-site workers.

Air Monitoring Activity: The air sampling consisted of three downwind stations in the yards of residences, two stations downwind of site at the site fence line, two background stations, and one mobile station. Each station consisted of various personal sampling pumps equipped with various collection media tubes- carbon, porapak-T Tenax/chromosorb (for GC/MS analysis), and GC-Tenax for on-site thermal desorptions GC analysis. The plan also called for performing real-time monitoring for organic vapors with hand held instruments.

The on-site GC analysis was used to screen samples to assist site personnel in determining if site activities were causing a release into the community. In addition, this information was used to select what tubes would be sent to an analytical lab for analysis. Lab samples were kept cool with the use of cool packs, which use an endothermic reaction for cooling. The chemicals are mixed by crushing the bags with ones hands. But after long hot days, using various types of protective clothing and equipment the easiest jobs become difficult. One of those bags just would not crush, so one of the samplers put the bag between his knee and with both hands and legs tried crushing the bag. The bag not only crushed but ruptured spraying his groin with the endothermic solution. The individual ran the 100 yards to the decon station in a world record pace. In addition to the burning sensation, the individual had to face the fact that he is the Team's Health and Safety expert.

E. TRAIN DERAILMENT: Gulf States

Site Description: This response activity was located in a rural area located in one of the Gulf of Mexico States. It consisted of approximately 40 derailed chemical tank cars, which were on fire, leaking and/or exploding.

ERT Support Function: In addition to the ERT's Air Monitoring and Occupational Health and Safety function, the team was also involved in evaluating soil and groundwater contamination, as well as cleanup techniques.

Air Monitoring and Occupational Health and Safety Activities: While this response left many memorable experiences, the following three are still dear to the authors' hearts.

1. Weather Balloons: The problem was that the air surveillance team was not able to get close enough to the air plume because of the explosion potential. Two small weather balloons were obtained from a nearby airport to lift the air collection pumps and tubes approximately 200 feet to get above the pine tree and into the plume. However, the two small weather balloons did not provide enough lifting power, so latex rubber gloves were filled with helium to assist. Imagine if you will, the gloves expanded to the size where they resembled cow udders. Yes, the press had a good time.

Unfortunately, the balloon/glove stations were set out at approximately 6:30 a.m. and left out for four hours. When the sampling team returned, the helium had expanded and exploded the gloves which brought the pumps crashing to the ground. The good news was that after approximately a 200 ft. free fall, the pumps "kept on ticking".

2. 110 Electric Generators: Since air monitoring at a derailment is often a 24 hour effort, the air surveillance team decided not to use the battery capabilities of the field gas-chromographs (GC's). Instead, the instruments were run off of the command post's gas generator. A surge occurred in the electricity, and blew out one of the two available field GC's. After this response, our analytical instruments have never been run off of generated power again.

3. Eye Protection: One of the chemical tank cars had leaked into a nearby drainage ditch. The material was very acidic and small pools were being cleaned up.

The authors had not only advised but were demanding that the ditch cleaners wear full face respirators. Of course, the Railroad's cleanup contracts Industrial Hygienist did not agree, and the issue of EPA's authority to enforce health and safety protocols during a State lead responsible party cleanup was being debated. During this 24 hours heated discussion, a ditch cleaner, who was wearing a 1/2 face respirator with no eye protection, lost his balance. In losing his balance, the shovel fell into the muddy pool containing the waste material, and he received a chemical burn in one eye.

7. MALATHION FIRE: Sri Lanka

Site Description: It was two weeks before Christmas and all through the office not a hazard was stirring not even a spill.

The quietness was broken when a call came over the hotline. The call was from the State Department AID office. They requested information on malathion, because a warehouse fire had just occurred in Colombo, Sri Lanka. The warehouse contained approximately 20 million pounds of malathion. This malathion was a wettable powder stored in corrigated cardboard boxes.

ERT Support Function: Initially, they wanted information on possible breakdown products, adverse health effects, and disposal options. A report was prepared immediately which contained the above information. We also informed them that the fire was probably smouldering at the bottom of the piles due to the fact that the boxes were stacked 20 feet high.

After the information was reviewed by the AID office, it was determined that ERT personnel were needed to perform an on-site inspection to assist the Sri Lankian Government in determining if the fire was still smouldering, whether vapors were still being released, and to determine appropriate disposal options.

Response Activity: The travel itinary for the two-man team consisted of a morning flight to Washington, DC for a briefing, and an evening flight to Sri Lanka.

The minor problems which occur with many responses started almost immediately. The sampling equipment had to be carried as luggage and this consisted of 12 pieces. The equipment consisted of temperature probes, cannister air purifying respirators, disposable protective clothing, air sampling and monitoring equipment, hand augers, and reference materials. During the trip to Sri Lanka this luggage had to be transferred between four planes (New York - Washington - New York - Switzerland - Sri Lanka). Only one piece of luggage was lost during this part of the trip.

Upon arriving at the airport on Friday morning the team found out that no reservations were made and seats were not available on the 7:00 a.m. flight. Next, the flight from New York to Switzerland was changed by the airlines at the last minute to a flight to Hamburg, Germany with a connection to Switzerland. This minor change caused a five hour delay in the teams' arrival in Sri Lanka. During the briefing the team had learned that some terriorist problems existed in the country. Upon arrival in Sri Lanka the team members observed that army personnel were guarding the airport and government offices. After talking to a local official, they learned that the head of State of Pakistan was visiting and the soldier was an honor guard.

Even with these minor problems the overall response went very well. The team was able to core into the pile to obtain temperature readings and measure vapor levels. The temperature probe showed that some of the piles were still smoldering, and the vapor readings revealed that no immediate health threat existed. The team also provided recommendations for disposal of the waste materials. The Sri Lankian people were extremely cooperative and cordial to the team during their stay.

Acknowledgement:

The authors express their appreciation to all members of the U.S. EPA, Environmental Response Team, U.S. EPA-ERT's TAT and U.S. EPA EERU contractors for their many contributions and constant updating of our response activities.

Conclusion:

The authors hope you have enjoyed their efforts to share those situations which have added to their learning experience. As in other fields, there is no substitute for hands-on experience in the hazardous materials response field.

A COMPUTER MODEL SYSTEM FOR CERCLA TYPE A DAMAGE ASSESSMENTS

Mark Reed[1]
Deborah French[1]
Thomas Grigalunas[2]
James Opaluch[2]

1) Applied Science Associates, Inc., Narragansett, RI 02882
2) Eonomic Analysis, Wakefield, RI 02879

ABSTRACT

A coupled marine transport/biological-injury/economic-damages model system has been developed to serve as the proposed basis for type A (small scale) damage assessments under CERCLA. The model, which operates on a personal computer, relies on large chemical and biological data bases for fundamental parameters. Spilled material concentrations are computed dynamically on the water surface, in the upper and lower water column, and in the sediments. Biological losses due to direct toxic effects on adults, and future catch reductions due to losses of larvae and juveniles, are calculated for commercially important species. Losses resulting from primary and secondary productivity are included through a simple fractional rule for energy transfer efficiency up the food chain.

INTRODUCTION

Potential environmental effects of chemical spills prompted passage by the United States federal government of the 1980 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). This act allows for polluter compensation to public and private parties for costs associated with spill response, as well as resulting natural damages. CERCLA regulations also provide for two types of damage assessment methodologies: type A, standard simplified procedures requiring minimal field observations, and type B, more complex and detailed studies for conducting assessments in situations which warrant further attention. This paper describes a numerical model system implemented on a microcomputer to perform physical fates, biological impact, and economic damage estimates for type A chemical spills. The entire model system and data bases are described in more detail elsewhere (Economic Analysis and Applied Science Associates, 1987).

MODEL SYSTEM DESCRIPTION

The proposed model system (Figure 1) is composed of three major components: physical fates, biological effects, and economic damages. The user enters information to characterize the spill: chemical identification number and amount spilled. The model obtains a set of chemical parameters from the chemical data base, which presently consists of over 450 substances including crude oils and petroleum products. These parameters, which are

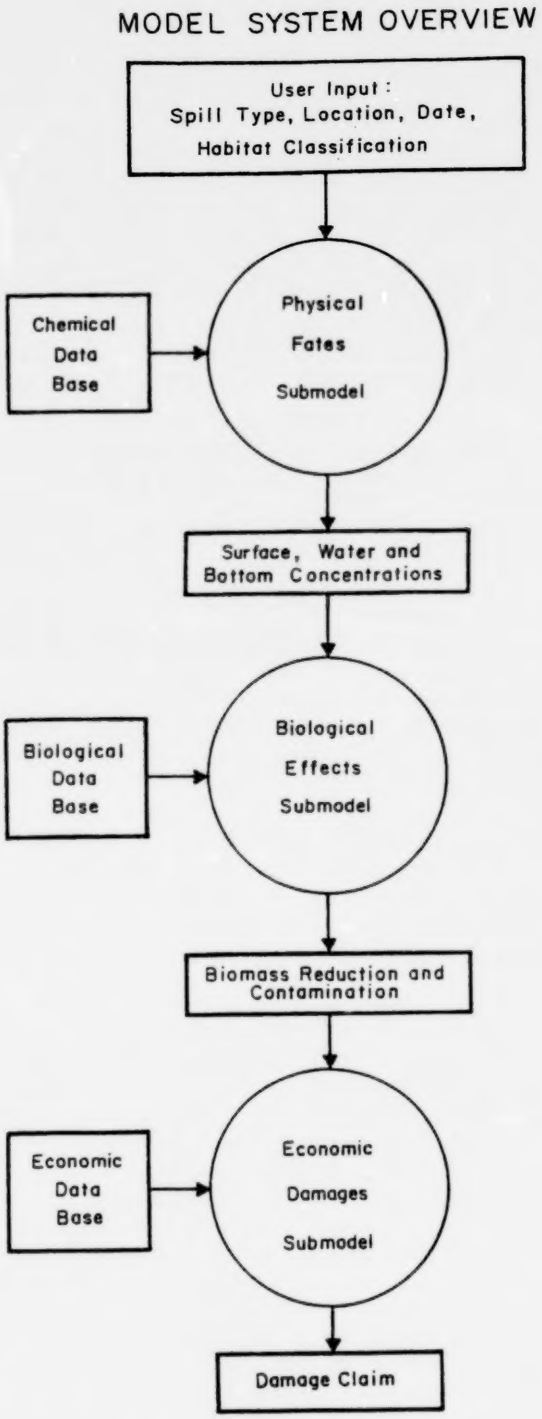
MODEL SYSTEM OVERVIEW
User Input: Spill Type, Location, Date, Habitat Classification
Chemical Data Base
Physical Fates Submodel
Surface, Water and Bottom Concentrations
Biological Data Base
Biological Effects Submodel
Biomass Reduction and Contamination
Economic Data Base
Economic Damages Submodel
Damage Claim

Figure 1. Model System schematic showing relationships among the submodels and data bases.

required to run the physical fates model, include density, solubility, molecular weight, adsorbed/dissolved partitioning coefficient, and vapor pressure. Based on these parameters, the submodel determines how much of the spilled substance evaporates into the atmosphere, spreads as a surface slick, is dissolved in the water and settles to the bottom. For petroleum spills which form surface slicks, values of viscosity and surface tension are also required and are included in the chemical data base. Degradability, solubility, and toxicity, plus environmental transport parameters, determine the duration and spatial extent of biological effects.

The physical fates submodel simulates the dispersion of the pollutant on the sea surface (as a slick), in the upper and lower water column, and in the sediments. A surface slick spreads and is transported by wind and currents, with continual evaporation into the atmosphere, and entrainment and dissolution into the water column. If the slick meets a shoreline, it is assumed to collect there.

A spilled substance entrained or dissolved into the water column is dispersed by mixing and is transported by currents. A portion of the dissolved substance may be adsorbed by suspended particulate matter. These particles will sink to the bottom at a certain rate, and in this way dissolved substances will reach the sediments. A heavy substance will sink directly to the bottom. The material which reaches the seafloor is mixed into the sediments using a simple mixing model. The submodel also includes evaporation from the dissolved state into the atmosphere.

If a spill occurs in the intertidal zone, the model asks the user to input shoreline type, and computes area of intertidal zone affected.

The water column is divided into two layers, upper and lower, so that different densities may be specified in each to simulate stratified conditions. The physical submodel assumes a set of default values for mean and tidal current velocities, average wind speed, density and concentration of suspended particles. The user has the option to change these values if more specific information on the site in question is available.

The submodel allows for cleanup of spilled materials. Cleanup is defined as the removal of chemical mass from the environment, and does not include such actions as the addition of dispersants to oil spills.

The physical fates submodel calculates concentrations in space and time in each of the layers (depth zones): upper water, deep water, and sediments. The area covered by a surface slick (if applicable) also is calculated. This information is passed to the biological effects submodel, which then calculates the biological effect of those concentrations.

The biological effects submodel receives data from three sources: the physical fates submodel, the toxicological section of the chemical data base and a biological data base. The biological effects submodel calculates both the short-term and the long-term biomass loss, passing these data to the economic damages submodel. Short-term biological losses can fall into two categories: death of adult organisms and lost productivity. Long-term losses treated by the model include lost recruitment due to larvae and juveniles killed, and lost growth of adults killed.

Death of adult organisms is calculated as follows: an LC50 value (lethal concentration to 50% of the organisms exposed to a chemical for 96 hours) and threshold value (concentration below which no (<1%) mortality occurs) are obtained from the chemical data base. The area versus concentration of spill is received from the physical submodel and the biomass of each species (for species having direct economic value, as grams wet weight per square meter) is received from the biological data base.

The biological submodel uses these values to calculate the biomass of each species killed (mortality is highest at the center of a spill, where concentration is highest, decreasing outward until the threshold concentration is reached). The submodel not only calculates mortality over area, but over time, until such time as concentration of the spilled chemical has everywhere fallen below threshold concentration. If an area is closed to fishing due to a spill, the submodel treats biomass within that area as catch loss, but it is not considered dead and not included in long-term losses of catch.

Organisms which are killed in a spill, but which have no direct economic value, are accounted for in a productivity, or food chain, section of the biological effects submodel. Plant EC50 values (pollutant concentration which reduces growth rate by 50%) are passed from the chemical data base, enabling calculation of lost primary (phytoplankton or other plant) production. This loss is passed partially through zooplankton (small animals inhabiting the water column), partially through the benthos (bottom-dwelling animals), and is ultimately expressed as a loss of economically valued species (by biomass) due to loss of potential food. Direct losses of zooplankton are also calculated and passed through the food chain to calculate resulting upper trophic level losses.

Surface slicks and intertidal spills are special cases. The physical fates submodel calculates the area of the slick (e.g., oil) which is multiplied by the number of birds and mammals (by species) per unit area to give total individuals affected. In the case of an intertidal spill of a petroleum product, the physical fate submodel calculates the area and time of impact. Intertidal spills of other chemicals are not treated by the physical submodel. The user gives the area of shoreline affected and the biological submodel totals the biomass (by species) affected.

Long-term losses include only lost recruitment of larvae and juveniles into the adult population, and lost future growth of adults. More complex changes, such as alterations of food chains, and chronic effects, such as loss of reproductive potential, are not considered. Such changes require more data to model than are currently available and, in any case, would presumably not result from small spills.

The recruitment and growth section of the biological effects submodel is based on accepted fisheries models. Larval survival rate, natural and fishing mortality rates, growth rate, and longevity are used to calculate the biomass of each species which would have been caught in the future but instead was killed by the spill. These losses (excluding the species biomass which would have died naturally) are calculated by species by year and passed to the economics model.

Certain characteristics of the spill location (input by the user) define one of a number of ecosystem types. Each ecosystem type has a data set which includes adult biomass (g/m^2 and larval numbers (no./m^2 for each economically valued species, by season, used in calculating direct mortality. The data base also includes primary, zooplankton and benthic productivity (by ecosystem type by season) and fisheries parameter estimates (growth, mortality, etc.) by ecological group (e.g., planktivorous fish; bivalves) used in calculating lost recruitment and growth.

For each chemical in the data base, the physical chemical properties supplied are: density (g/cm^3), solubility (mg/l), molecular weight (g/mole), degradation rates (in water and in sediments, per day), vapor pressure (atm), and adsorbed/dissolved partition coefficient. The toxicological data supplied includes: LC50 values (for phytoplankton, zooplankton, fish, benthos, and ichthyoplankton (larvae fish and eggs) in parts per billion (ppb) and a threshold effects value (ppb). A standard bioeconomics model is used to derive the measure of damages to commercial and recreational fisheries. The short-term and long-term and direct and indirect injury to fish which would have been harvested in the absence of the incident is an output of the biological effects submodel. Injured species are allocated between commercial and recreational uses, given estimates of the relative weight of recreational and commercial landings, by species, for each region and of the total fishing mortality rate (natural and fishing mortality) for species groups. Ex-vessel (price at the dock) fish prices, averaged over three years, are used to evaluate damages to commercially harvested fish. Price information for commercial fisheries and catch data for commercial and recreational fisheries are from National Marine Fisheries Service sources. Values for recreational sports fishing are adapted from the literature.

Damages resulting from injury to lower trophic, non-commercial organisms are based on the ultimate loss in the *in situ* use value of predator species (commercial and recreational fisheries, waterfowl and shorebirds, and marine mammals) which occurs when an incident affects the productivity of the food chain. The food chain or ecological model developed in the biological effects component of the ocean systems model quantifies the biological injuries which arise over time as a result of the incident. Given the quantification of biological injuries, damages are measured using the concepts and data applicable to commercial and recreational fisheries, to waterfowl and shorebirds, and to marine mammals.

Injury to waterfowl and shorebirds results in losses of consumptive (hunting) and non-consumptive (e.g., viewing, photographing) *in situ* use values. The quantification of biological injury to waterfowl and shorebirds is an output of the biological effects submodel. Damages resulting from consumptive use value losses are measured using available estimates of the marginal value of an additional waterfowl (duck or geese) harvest. Damages arising from non-consumptive use value losses for non-game species are measured by employing an estimate of the marginal change in visitor days associated with a change in bird population for a wildlife refuge. The resulting estimate of lost visitor days then are evaluated based on a unit day value published by the Water Resources Council.

Damages caused by injury to public beaches are measured by the lost *in situ* use value and depend upon the season, the type of public beach affected and the extent and duration of the injury. The user specifies the location and season of the incident, the type of beach affected (national or other public beach), and the amount and substance spilled. For oil spills, the physical fates submodel determines the extent of beach impaired and the time to removal by natural processes. If cleanup operations are carried out, the user must specify the time of cleanup and the quantity removed. For spills of other substances, the user must specify the length of beach affected and the time to recovery either through natural processes or cleanup.

EXAMPLE APPLICATIONS

To demonstrate model system output, we include some hypothetical oil spill damage assessments for an estuarine and offshore location in the Arcadian (i.e., Cape Cod to Nova Scotian) area. To simplify comparisons, we have assumed no coastal impacts in either location. Other parameters for the two cases are shown in Table 1.

Value	Parameter Name
0.1	Mean Ocean Surface Current (m/sec)
0.5	Tidal Velocity (m/sec)
0.1	Tidal Velocity (m/sec)
5.0	Mean Wind Speed at Spill Event (m/sec)
0.0	Wind Direction (degrees)
20.0	Depth of Upper Water Column to Pycnocline (m)
20.0	Depth of Lower Water Column to Bottom (m)
10.0	Air Temperature (degrees C)
12.0	Water Temperature (degrees C)
1.0	Suspended Sediment Concentration (mg/l)
10.0	Suspended Sediment Mean Settling Velocity (m/day)

Table 1. Physical environmental parameters for example model system applications.

The results of these example applications are summarized in Figure 2 for the estuary and Figure 3 for the offshore. First, it can be seen from the damage scales that the seasonal variability at either location is at least as important as the differences between the two locations. These latter differences are due mainly to the higher productivity levels associated with estuaries, as well as to the higher commercial values of the organisms impacted. Second, seasonal variability in the estuarine environment exceeds that offshore, reflecting the spring and summer use of estuaries as spawning and nursery areas by many commercial species. Finally, the relationship between spill volume and damage is weakly non-linear, increasing from 20:1 (metric tons spilled: thousand dollars damage) at the 500 mt level, to 16:1 at the 1000 mt level in the August estuarine case (Figure 2). Because the oceanographic parameters have been held constant between the two applications (Table 1), the observed behavior can be attributed to the juxtaposition of non-linear physical dispersion magnified by the density of pelagic biota in

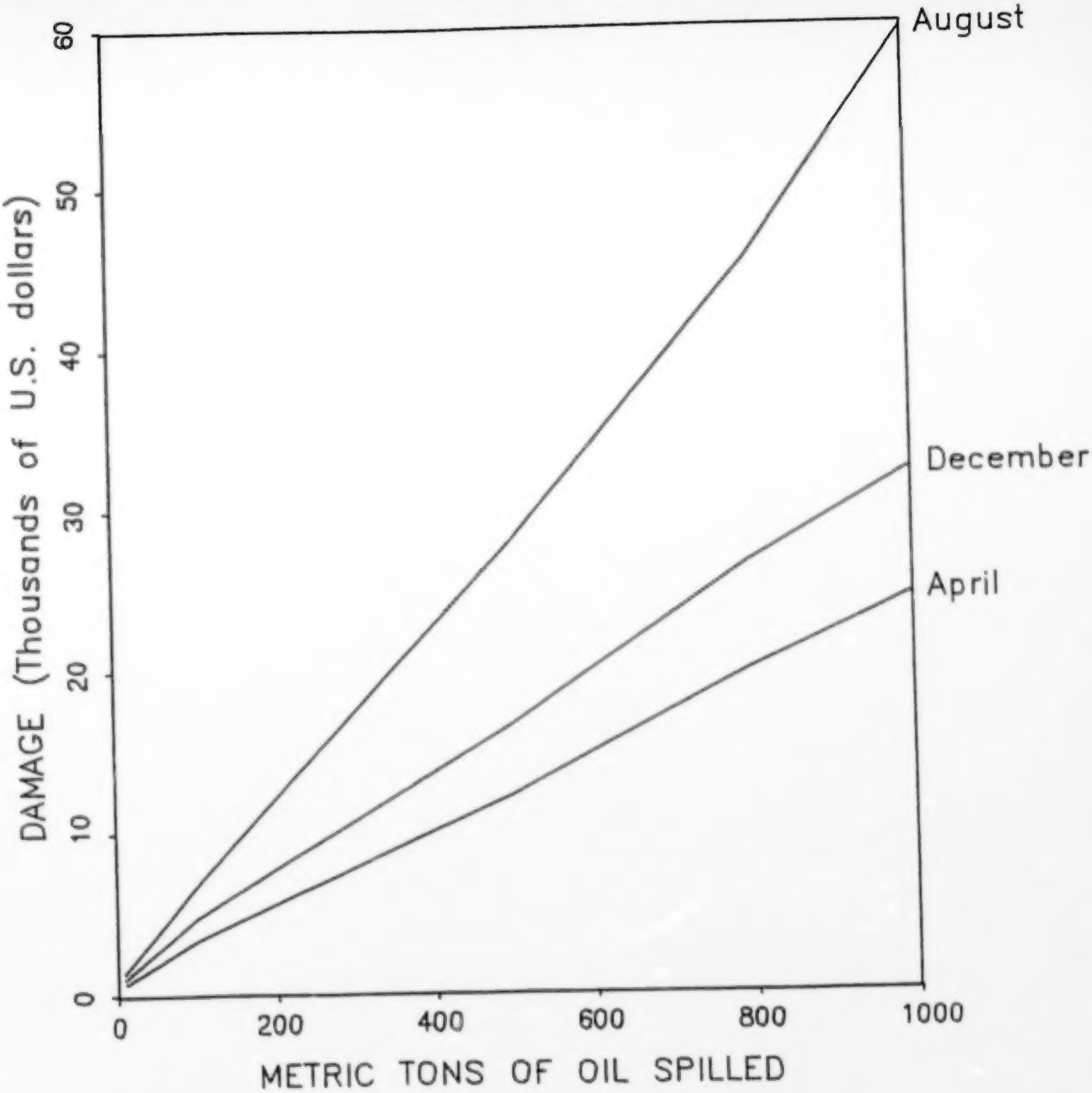

Figure 2. Damage assessment (U.S. $) for spills of light crude oil in an estuary on the Northeast coast (Massachusetts to Nova Scotia).

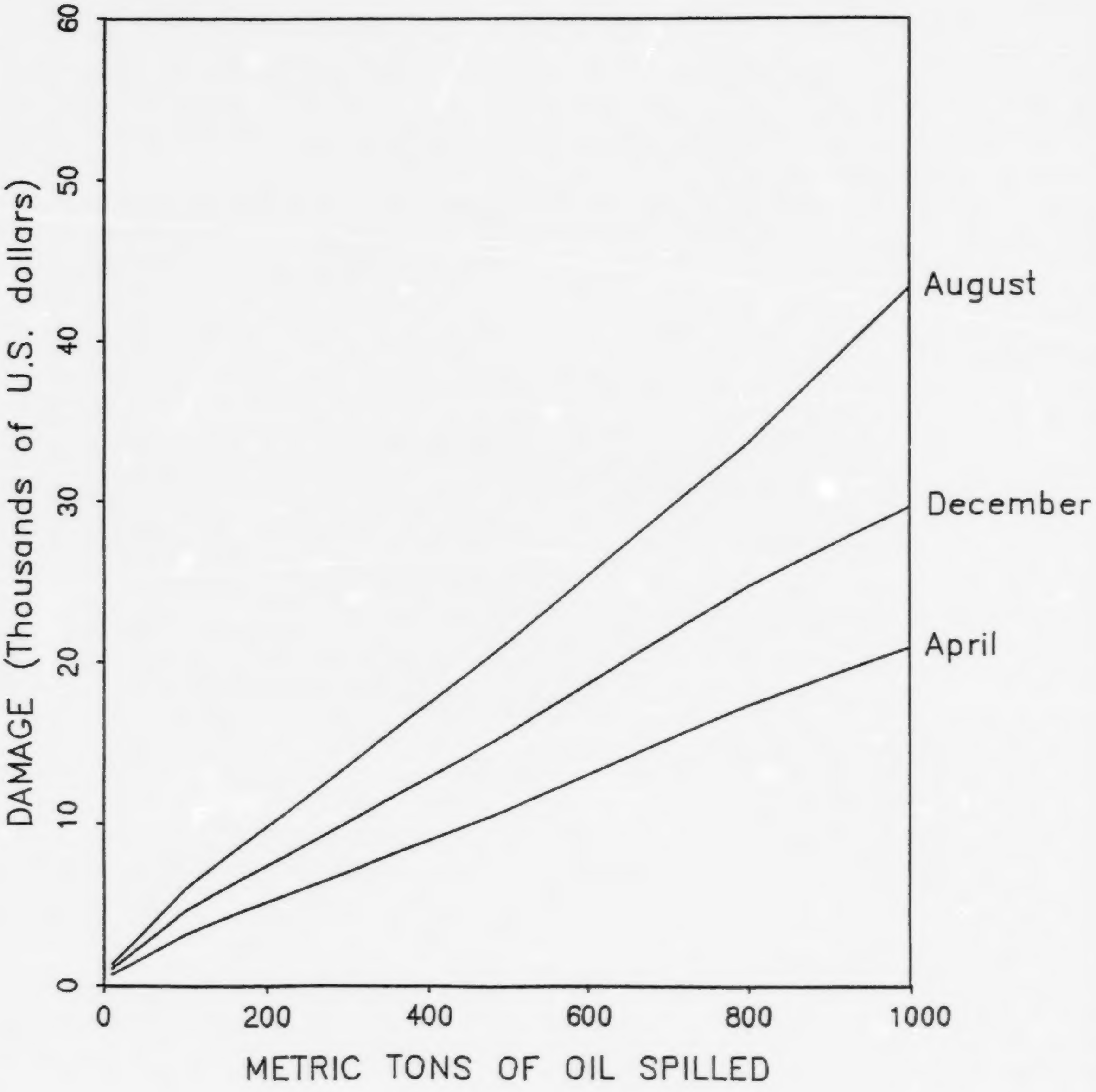

Figure 3. Damage assessments (U.S. $) for spills of light crude oil in the Northeast offshore area.

the two areas. For details of model formulations and capabilities, we refer the interested reader to the final report for the project.

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DISCLAIMER

The opinions, findings, conclusions, and recommendations expressed in this paper are those of the authors, and do not necessarily reflect the views of the U.S. Department of the Interior.

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Ethylene Dichloride/Ethylene Glycol Spill In a Major Water Resource in British Columbia

Kenneth L. Christian William P. Moorehead

ABSTRACT

In March, 1982, a Canadian National Railway train containing hazardous chemicals derailed near Blue River in the interior of British Columbia, Canada. Significant quantities of ethylene dichloride and ethylene glycol were released into the North Thompson River. The local Public Health authority's role in response to this spill is discussed as it relates to the potential threat to domestic water supplies. Tables depict the movement of the ethylene dichloride through the river system. Discussion includes recent research regarding ethylene dichloride.

* * *

On March 3, 1982 at 3:20 p.m., a Canadian National Railway (C.N.R.) train containing hazardous chemicals derailed approximately 13 km south of Blue River, British Columbia. Of the 25 cars that derailed, two contained sodium hydroxide, seven contained ethylene glycol and 16 contained ethylene dichloride. The following volumes of product were released into the North Thompson River, a major water source in British Columbia: Ethylene dichloride - 628,700 litres, Ethylene glycol - 223,200 litres.

The local detachment of the Royal Canadian Mounted Police (R.C.M.P.) responded to the derailment at 3:43 p.m. and the 911 Kamloops emergency telephone center informed Provincial Emergency Programme (P.E.P.) personnel of the accident. The C.N.R. transmitted information internally and notified Dow Chemical at Fort Saskatchewan, Alberta, producer of the chemicals. Agencies with administrative responsibilities had been informed of the spill, including the Medical Health Officer, in view of the public health concern.

A public announcement was made on local radio with a rebroadcast unit in the area of immediate risk warning water users in the area to discontinue using the water until the situation could be clarify. This information was also transmitted locally by the P.E.P. coordinator and the R.C.M.P.

The response time to the accident was excellent in view of the bad weather conditions, limited access and geographical location. Within one hour the site was determined to be stable and all persons at the accident scene were safe. The first priority was to develop access to the site, bring response teams to the area and maintain occupational safety for workers.

Occupational health and safety, security and management of the spill remained the responsibility of the C.N.R. with technical support from the Dow Chemical response team through a field command center at Blue River and on site. Provincial and Federal Environment personnel monitored the location during the 10 days of clean up. The local Medical Health Officer assumed a leadership role outside the immediate spill area because there was a danger of a domestic water source being polluted with potentially toxic amounts of chemical.

The characteristics of a disaster in British Columbia determine which agency assumes leadership, interfaces with the news media and the public to establish confidence and disseminate accurate and balanced information. Of immediate concern in the management of this spill were:

A. Extent of the spill;
B. Characteristics of the chemicals, their toxicity and potential hazard to human and animal health;
C. Interaction of the chemical spill with the environment;
D. Identification and notification of water users;
E. Characteristics and condition of the river in relation to dissemination of chemical;
F. Time factors in relation to the decision-making process and availability of accurate information;
G. Development of liaison and a climate of trust with the organizations involved.

The physical and chemical characteristics of ethylene dichloride and ethylene glycol are shown in Table 1.

The solubility of ethylene dichloride and its weight in relation to water suggested initially that it might provide particular problems to water intakes. This concern was dispelled by subsequent data (Tables 2 and 3). The solubility and volatility of the ethylene dichloride played an important role in its dissipation, minimizing public health concerns.

Table 1

Physical and Chemical Properties of Ethylene Dichloride and Ethylene Glycol

	1. Ethylene dichloride (10)	2. Ethylene glycol (11)
PHYSICAL STATE	A colorless, oily liquid with a chloroform-like odor, detectable over the range of 6 to 40 ppm, with a sweet taste.	A colorless, odorless, viscous, hygroscopic liquid with a bitter-sweet taste.
MOLECULAR WEIGHT	98.97	62.07
BOILING POINT	83.5°C	197.6°C (760 mm.Hg)
PERCENT IN "SATURATED" AIR	11.5 (25.5°C)	0.0131 (25°C): 0.0079 (20°C)
SOLUBILITY	0.9 g/100 ml water at 20°C: soluble in ethanol, ethyl ether	Miscible with water
FLASH POINT	18.3°C (open cup); 130°C (closed cup)	121°C (TOC)
SPECIFIC GRAVITY	1,2529 (20/4°C)	1.1133 (20/4°C)
REFRACTIVE INDEX	1.4443 (20°C)	1.4316 (20°C)

No sodium hydroxide was spilled in the derailment. Concern regarding the ethylene glycol that was spilled was short lived for the following reasons:

A. Ethylene glycol is completely soluable in water;
B. The North Thompson River provided a high dilution factor relative to the volume spilled;
C. Initial calculations indicated that concentrations would be so low as to tax analytical capabilities of available testing equipment;
D. The toxicity of ethylene glycol was not significant compared to the ethylene dichloride which was spilled;

Most communities in the North Thompson area use tributaries as their source of raw water because of the seasonal turbidity of the North Thompson River. North of the confluence of the North and South Thompson Rivers, there is a population of approximately 10,000. However, only 2,530 people who receive their drinking water directly from the river were potentially at risk of having their water supply affected by the spilled chemicals (Table 4). Vavenby, with a population of 490 people 67 km. south of the derailment was the community at immediate risk. Water systems for 80 km. downstream of the spill were closed by 7:00 p.m. March 3 and water was shipped in by the C.N.R. Other public systems further downstream were not closed at this time.

By March 6, three days after the spill, laboratory data gave evidence of taste and odor concerns in the lower reaches of the river. It appeared that the taste and odor threshold of 22 ppm for ethylene dichloride might be exceeded. Consequently, a decision was reached to order the closure of the remaining water intakes along the river for 48 hours. This decision was arrived at essentially to avoid public anxiety and panic. C.N.R. again provided water to all persons affected.

Table 2

Initial Response Results

Concentration of ethylene dichloride (ppm(w/w)) in North Thompson River following derailment March, 1982

Town location miles downstream from derailment	Sample location miles downstream from derailment	Mar. 4	Mar. 5	Mar. 6	Mar. 7	Mar. 8
	0.1	11	8	6	10	3
	4	32	4	—	—	—
	8	25	5	7	4	—
	12	90	14	—	—	—
Avola	16	ND	45	—	—	—
	20	ND	80	—	—	6
	24	—	—	—	—	—
	28	—	220	12	15	—
	32	—	180	—	—	—
	36	—	—	18	—	—
	38	—	ND	—	10	—
Vavenby	44	—	—	—	—	—
	48	—	—	—	—	—
	52	—	ND	33	18	—
	56	—	—	—	—	—
Clearwater	60	—	—	40	—	—

TABLE 2 (CONTINUED)

	64	—	—	—	13	2
	68	—	—	19	—	3
	72	—	—	—	8	—
Little Fort	76	—	—	—	—	—
	80	—	—	12	14	3
	84	—	—	—	—	—
	88	—	—	ND	14	9
	92	—	—	—	ND	—
Barriere	96	—	—	ND	ND	10
	100	—	—	—	—	—
	104	—	—	—	—	—
	108	—	—	—	—	3
	112	—	—	—	ND	—
	116	—	—	—	—	—
	120	—	—	—	ND	1
	124	—	—	—	—	—
Rayleigh	128	—	—	—	ND	ND
	132	—	—	—	—	—
	136	—	—	—	—	—

ND — not detectable less than 1 ppm (w/w) EDC

Table 3

Follow up Monitoring Results in North Thompson River Following Derailment March, 1982

Concentration of ethylene dichloride (ppm(w/w))*

	March 8	9	10	11	12	13	14	15	16	17	18
33 miles south of Blue River (near Avola)	—	1.8	1.3	1.5	—	—	—	0.39	—	0.37	—
Weyerhaeuser Vavenby	10*	2.3	0.69	0.87	0.005	0.49	0.38	0.005	0.005	0.10	0.037
Barriere Bridge	—	2.0	0.65	0.53	0.48	—	—	0.130	0.005	0.030	0.016
Rayleigh Water	—	0.005	0.005	1.4	1.2	—	—	0.19	—	—	—
Kamloops Overlander Bridge	—	—	1.3	1.3	0.85	—	—	0.110	0.060	0.090	0.0027
Kamloops Woodland Trailer Park	—	—	—	—	—	0.38	0.19	—	—	—	—
Savona	—	—	—	—	—	—	—	0.005	0.005	0.005	0.005

	March 19	22	24	25	26	April 5	14	19	26	May 3
33 miles south of Blue River (near Avola)	0.20	0.14	0.17	—	0.170*	0.080	0.041	0.041	0.021	0.015
Weyerhaeuser Vavenby	0.08	0.056	0.59	—	0.110	0.025	0.024	0.014	0.008	0.007
Barriere Bridge	0.020	0.015	0.011	—	0.007	0.005	0.005	ND	ND	ND
Rayleigh Water	—	—	—	—	—	—	—	ND	ND	ND
Kamloops Overlander Bridge	0.022	0.011	0.007	—	0.005	0.005	0.005	ND	ND	ND
Kamloops Woodland Trailer Park	—	—	—	—	—	—	—	—	—	—
Savona	0.005	0.005	0.005	0.005	0.005	0.005	—	0.005	0.005	0.005

ND — Not Detectable

Table 4

Water Systems and Populations at Potential Risk*

Location	Population Affected	Miles from Derailment	Elevation Feet
Wreck Site	0	0	2100
Vavenby Community Water Supply	96	41	1450
Vavenby Improvement District	400	42	1400
Black Pines Water System	70	121	1200
Noble Creek Water System	100	123	1175
Maple Ridge Water System	20	125	1160
Rayleigh Waterworks	1750	127	1150

* In addition, it was estimated that there were 30 independent systems servicing houses and farms, involving an additional 100 persons plus livestock.

This move closed the river from the spill site to the confluence of the North and South Thompson Rivers in Kamloops some 200 km. south. The Canadian Water Survey records the mean annual flow of the North Thompson River at 150 cubic meters per second. Although no actual flow measurements were conducted at the time of the spill, it was estimated that flows were approximately 30 cubic meters per second as the spill occurred during a low water period. The velocity of the river is irregular due to the character and changing elevations (Table 4). Initial estimates of speed were 5 kilometers per hour calculated from the site of the derailment to the confluence of the North and South Thompson Rivers at Kamloops. This made predictions of the movement of the spilled chemical difficult. In the first 24 hours, the material had moved 16 km. from the derailment site; however, it moved an additional 40 km in the next 20 hours.

Much of the research regarding the reaction of ethylene dichloride in fresh water has been conducted utilizing water with a temperature of 5 degrees C or higher. The temperature of the North Thompson River was near 0 degrees C at the time of the spill and during the subsequent cleanup operations. In addition to the temperature, much of the river was ice-covered, thus reducing the dissipation of ethylene dichloride into the atmosphere.

These conditions made sampling difficult and somewhat dangerous. Initial samples were obtained by depth sampling with a VanDoren sampler suspended from a helicopter. Follow-up samples were obtained from bridges, water intakes or at patches of open water by depth sampling or dip sampling from the river bank.

The quality of the river water, as determined by chemical and bacteriological analyses, had been consistent over the past years and had met the Canadian Drinking Water Standards.

Discussion

Volatilization is the major transport process for removal of ethylene dichloride from aquatic systems (1). Other processes such as photolysis, oxidation, hydrolysis, biotransformation and biodegradation do not appear to play a significant role. Adsorption onto sediments is not a contributory factor in environmental spills, and it is not likely to bioaccumulate to any significant extent.

Ethylene dichloride may enter the body by ingestion, inhalation or skin adsorption. Acute poisoning may cause headache, dizziness, loss of consciousness and ultimately internal bleeding and death. Recurrent exposure produces gastrointestinal symptoms, eventually liver and kidney failure and possible death. From animal studies, it appears that a single exposure of 100 ppm would cause no symptoms or damage. At 300 to 400 ppm, symptoms should become evident and tissue damage may occur in humans. It is significant to note that ethylene dichloride concentrations at low levels in water would render the water distasteful to humans and animals. There is little if any possibility of an adult accidentally or unknowingly ingesting a harmful quantity of ethylene dichloride in water.

Ethylene dichloride has been manufactured extensively throughout the world, 80% of which is used in the production of vinyl chloride. Widespread use has led to its being identified frequently in raw and finished water (3,15).

Research conducted by the U.S. National Cancer Institute indicates that ethylene dichloride is carcinogenic in rats (13). Other ongoing studies suggest that the carcinogenity of ethylene dichloride may be overstated (2, 10, 12), and there are continuing arguments on the mechanisms of tumor formation and the applicability of animal studies to man (4, 6, 14). The involvement of a public water supply, though, makes it necessary to address the carcinogenicity issue.

The U.S. Environmental Protection Agency has proposed human health criteria for chlorinated ethanes (14). The criterion for ethylene dichloride is based on the high dose (107 mg/kg body weight, 5 days per week), which induced mammary adenocarcinomas in female rats. Using a linear, non-threshold model and including the consumption of fish from chloroethane contaminated waters, the criterion for ethylene dichloride is 7 ug/l. A safety factor of 1000 is used in the calculation assuming a body weight of 70 kg. The model assumes a risk of 1 in 100,000 of developing cancer as a result of drinking 2 liters of water per day containing a concentration of 7 ug/l along with the allowances for eating fish.

The interaction of the chemical spill and the environment is shown in Tables 2 and 3. Sampling from the North Thompson River indicated the criterion of 7 ug/l was reached with eight weeks. The Fisheries Department of Environment Canada reported no fish kills, and the spawning beds apparently remained undisturbed from the C.N.R. spill.

The development of liaison and a climate of trust with the leading organizations involved was essential. Telephone communication with Dow Chemical, C.N.R., Ministry of Environment and the local Medical Health Officer was initiated within two hours of the derailment. A continual flow of information and open and frank discussions occurred. The Medical Health Officer was free to make decisions on the basis of Public Health without pressures from any quarter. Three major administrative meetings were held in addition to continual consultations with professionals, media and the public.

The first meeting March 4 at the field command post in Blue River dealt with the crash site and possible approaches to clean-up. The second meeting on March 6 in Kamloops included all agencies involved and two elected councillors of the City of Kamloops to represent the public interest. A thorough review of the accident, the chemicals, and available laboratory results led to the decision to remove other water systems at risk from the river for 48 hours. This meeting was followed by a press conference. An agreed statement was read and each representative was made available for questions. The third meeting March 8 reviewed all laboratory data to date. The concentration of chemicals at this time was regarded as safe, and the Medical Health Officer removed the restrictions on all water systems.

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The response to a spill such as this is a multi-faceted operation involving cooperation and assistance of all agencies concerned. The high level of cooperation and the climate of trust which evolved were essential to the effective response to the Blue River incident. The authors recognize the contributions of Gordon Bute, Dow Chemical Co., Murray Dyer, Provincial Emergency Programme, British Columbia Ministry of the Environment; Ken Evans, Waste Management Branch, British Columbia Ministry of the Environment; Tim Johnstone, Director of Epidemiology, British Columbia Ministry of Health; Robert Lutz, Dow Chemical Co.; Alex Rennie, Canadian National Railway.

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Ken Christian A.Sc.T, CPHI(C) is a Public Health Inspector with the South Central Health Unit in Kamloops, B. C. Bill Moorehead M.B.,Ch.B.,M.Sc. FRCP(C) is the Medical Officer of Health with the South Okanagan Health Unit in Kelowna, B. C.

Compound Specific Detectors for Field Information

E.B. Overton and D. Kummerlowe
Institute for Environmental Studies, Louisiana State University
Baton Rouge, Louisiana
Hazardous Material Spill Branch National Oceanic and Atmospheric Administration,
Seattle, Washington

Modern laboratory analytical instrumentation possesses the inherent analytical capability to identify and quantitate a wide variety of toxic chemicals in various types of environmental samples. While these analytical techniques are quite sensitive and can identify specific chemicals at trace levels, they require the services of a fully equipped laboratory and are quite time consuming. At the other end of the analytical spectrum are small, rugged, portable instruments that can be used in field situations. However,these instruments do not possess the analytical capability to identify and quantitate specific toxic chemicals at trace levels. The instrument development project of the Hazardous Material Response Branch - National Oceanic and Atmospheric Administration is designed to perform research that is necessary to produce chemical instrumentation that will bridge the gap between these two analytical extremes.

Specifically, the NOAA-HAZMAT project is developing instrumentation that can be used in field situations to identify and quantitate volatile toxic chemicals at trace levels (compound-specific analyses). Its goals include the development of "portable" analytical instrumentation that can produce "laboratory quality" analyses of volatile toxic chemicals with sensitivities in the low parts per million range (0.1 x TLV) and with short analytical response times. Further, the analytical devices must have the capability to transmit chemical data from remote field locations to a central laboratory facility for interpretation by a trained chemist, if needed.

Methods employed in the NOAA instrument development project include modification of off-the-shelf analytical equipment, originally designed for in-lab applications, to meet the needs of rugged, field deployable instrumentation. Since no single analytical device is universally applicable or capable of providing compound-specific field analyses for the wide variety of toxic chemicals in common use, five different types of chemical instruments were chosen for this development project. These include: a small portable microchip high resolution gas chromatograph (Michromonitor 500, Microsensor Technology Inc., Freemont, CA); a small, bench-top mass spectrometer (the Ion Trap Detector, Finnigan Instruments, San Jose, CA); a Fourier Transform infrared spectrometer (IBM instruments, Danbury, CT); a piezoelectric quartz microbalance (Quartz Sorption Detector, California Measurements, Sierra Madre, CA); and small portable gas chromatographs with electron capture and photoionization detectors (S Cubed, San Diego, CA and Photovac International, Thornhill, Ontario).

These instruments, which were not originally designed for field applications, are being modified and integrated with specially developed hardware, software, and analytical techniques to meet the needs for compound-specific analyses in field situations. Procedures have also been developed to use telemetry to transmit analytical data from field locations to a central laboratory, and to transmit instrument control information from the laboratory to the field. This allows data interpretation without the necessity of taking a trained chemist to the field. Thus, the basic concept that has evolved is to "take the analytical sensor to the problem" rather than "bring the problem to the sensor".

The instrumentation can be used in a variety of circumstances that require rapid analysis of toxic volatile chemicals at or below their toxic levels. Such instances include: toxic chemical spills; hazardous waste site evaluations; detection and fingerprinting of underground gasoline leaks; measuring fugitive industrial emissions; detection of indoor air pollution; monitoring toxic chemicals in remote environments; and others.

Currently, the instrument development project is field testing the microchip gas chromatograph and developing instrument user-friendly interfaces for data interpretation. Other instruments are in the prototype stage of development and not yet ready for field testing. This paper outlines results from several aspects of this instrument development project.

MICROCHIP GAS CHROMATOGRAPH

The Michromonitor 500 is a small portable microchip capillary column gas chromatograph with a thermal conductivity detector. It was designed by its manufacturers to be used for industrial hygiene monitoring of certain chemicals. Design considerations prohibit it from analyzing an air sample in a fashion that detects all pollutants in the sample. To overcome these limitations we have developed a user-friendly interface and software, using a Macintosh computer, which allows the user to take advantage of the significant analytical information in the entire capillary gas chromatogram. Additionally, because its run times are less than one minute, the microchip GC provides rapid analytical turn-around times.

The Macintosh-Michromonitor interface allows three modes of operation. In the first mode the user operates the Michromonitor from the Macintosh in the analytical mode that was designed by the factory. This mode can be useful for quantitative analysis when the identities of the pollutants are known. In the second analytical mode of operation, raw data are sent from the Michromonitor to the Macintosh, which produces reconstructed gas chromatograms on the computer screen for examination by a chemist. In the third mode of operation, data on retention times and peak areas are sent to the Macintosh which, in turn, calculates a retention index for each peak and identifies the vapors based on their retention index match with library index data. The retention index which we developed is essentially temperature independent. It is based on a modified Kovats index in which the retention times of the reference compounds are calculated at ambient temperatures rather than measured. Qualitative analyses are aided by using correlation chromatography techniques, in which the sample is analyzed on columns of different polarities. The Macintosh program is designed to be user-friendly, so that response personnel can operate the instrument in the field with relatively little training. Data can also be transmitted via phone lines and/or radio signals to trained chemists for interpretation.

MODIFICATION OF PHOTOVAC PORTABLE GAS CHROMATOGRAPH

The Photovac 10S50 is a very small, self-contained, portable gas chromatograph (GC) utilizing a highly sensitive photoionization detector (PID). As equipped from the factory, the GC contains a 1/8" x 6" pre-column and a 1/8" x 4ft. 5% SE-30 analytical column. This arrangement of columns allows operation in a "back-flush" mode in which mixtures of compounds are introduced into the instrument. At a predetermined time compounds which are of no interest and/or which might cause a very long run time are "back-flushed" and not allowed to enter the analytical column. We modified the instrument to make it a two column device by eliminating the pre-column and "back-flush mode" of operation. This allows separation of mixtures of very volatile components on a long column as well as separation of those components with a relatively low vapor pressure on a short column.

A conventional Photovac GC analysis of the volatile priority pollutants requires approximately 30 minutes of run time. Separation of the early eluting components is not adequate for identification. However, the sensitivity of the PID is certainly remarkable and thus allows applications of the Photovac GC for the analysis of low levels of certain compounds. If the optimum analytical parameters (flow rate of the column, sample injection size, creation of a library of compounds, etc.) for chromatography can be established in advance of actual field use, then the modified, packed-column Photovac can be used effectively for detection of low levels of trace chemicals.

The injection system and capillary column used with the microchip gas chromatograph was interfaced to the PID of the Photovac. Excellent sensitivity was obtained although the actual amounts of compounds entering the PID were substantially less than in normal packed column Photovac operation. The resolving power of the capillary column was not fully realized when used in conjunction with the PID. We feel that this was caused primarily by the detector cell volume which was not designed specifically for use with short capillary columns. Problems associated with the differences in ionization potentials of the various classes of compounds, i.e. aromatic compounds, halogenated compounds, and straight-chain alkane compounds also caused analytical confusion. However, use of a combined microchip gas chromatograph with a PID produced sensitive analyses with run times measured in seconds, rather than minutes. This significantly increases the capabilities of the instrument package for many quantitative detection applications.

MICHROMONITOR / ION TRAP DETECTOR SYSTEM

In keeping with the design philosophy of providing field usable instrumentation with rapid, laboratory quality analytical data, the Michromonitor/ITD (Ion Trap Detector) GC/MS (Gas Chromatography/Mass Spectrometer) combination has been developed. This instrument combines the speed and resolution of the microchip chromatographic system with the power and definitive compound identificating capability of a mass specific detector.

For analysis of volatile compounds, the system offers the combination of retention time data in addition to specific compound fragmentation information that is comparable with conventional "laboratory bound" GC/MS instruments. The relatively small physical size of the GC/MS system, and its response speed, makes it attractive for use in field situations.

The interfacing of the two instruments was accomplished by developing the capability to connect a capillary column from a micropack GC module into the open-split interface of the ion trap detector. Further system size reduction is seen to include mounting the microchip GC module into the cabinet of the ITD, use of a small "lap type" computer to run the ITD, and development of simple electronics (also mounted in the ITD cabinet) to enable simplified control of the microchip GC module.

The combined microchip GC-MS unit can identify volatile priority pollutants in less than two minutes and can detect benzene, with a recognizable mass spectra, at ambient air concentrations of 0.1 ppm.

CONCENTRATOR FOR FIELD INSTRUMENTATION

When analyzing hazardous chemicals in ambient air it is important to be able to detect the vapors of such chemicals at concentrations at or below their toxic levels (0.1 TLV). This means detection of vapors in the parts per billion range for many compounds. The Michromonitor is equipped with a thermal conductivity detector (TCD) which can generally detect most compounds in the parts per million range. Other detectors, like the Photoionization Detector, Electron Capture Detector, and Flame Ionization Detector, are more sensitive; but they are not 'universal', i.e. there are some compounds which they can not detect. The TCD lacks sensitivity, but has universal response. In order to detect pollutants at toxic ambient concentrations, we have developed a device which will concentrate vapors before analysis, effectively lowering the detection limits for the analyses.

The concentrator consists of two 'traps' which are small tubes filled with Tenax GC packing. A relatively large air sample (for example 50 ml) is passed through a trap at ambient temperature. The trap is then heated to 250ºC, and the desorbed organics flushed with a small amount of clean air (1-3 ml). Thus, the organics,which were originally in a large sample, have been concentrated into a smaller volume (in this case yielding a 50:1 concentration). The enriched sample can then be presented to the Michromonitor or MM-ITD for analysis. The elution volume of the concentrator is from 0.5 to 5 ml, depending on the volatility of the chemicals, and this allows more than one analysis of the enriched sample. Thus, it is possible to analyze the same concentrated sample on different columns or on different instruments. A concentrated sample can also be injected into the

Michromonitor/Ion Trap Detector (GCMS-like) unit for mass spectral analysis. With two traps in the concentrator, it is possible to use one trap while the other is cooling down, so that the sampling procedure is timely.

The concentrator also has a 'purge and trap' device which can be used to detect organic pollutants in water samples. Clean air is bubbled through 1 ml water samples, stripping the organics out of the water and depositing them on the trap. The trap is then desorbed in the usual way to obtain a sample that is ready for analysis.

This device differs from other concentrators in that the traps are permanently attached inside of the box and are used repeatedly, so that the performance of each trap can be verified and understood. Most concentrators use 'disposable' traps, which are used only once and discarded. Additionally, each sample can be analyzed more than one time, and this increases the confidence in identification of compounds by chromatographic methods.